

Review



# Visible-Light Photocatalysts and Their Perspectives for Building Photocatalytic Membrane Reactors for Various Liquid Phase Chemical Conversions

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**Abstract:** Photocatalytic organic synthesis/conversions and water treatment under visible light are a challenging task to use renewable energy in chemical transformations. In this review a brief overview on the mainly employed visible light photocatalysts and a discussion on the problems and advantages of Vis-light versus UV-light irradiation is reported. Visible light photocatalysts in the photocatalytic conversion of CO<sub>2</sub>, conversion of acetophenone to phenylethanol, hydrogenation of nitro compounds, oxidation of cyclohexane, synthesis of vanillin and phenol, as well as hydrogen production and water treatment are discussed. Some applications of these photocatalysts in photocatalytic membrane reactors (PMRs) for carrying out organic synthesis, conversion and/or degradation of organic pollutants are reported. The described cases show that PMRs represent a promising green technology that could shift on applications of industrial interest using visible light (from Sun) active photocatalysts.

**Keywords:** photocatalytic membrane reactor; photocatalytic membrane; photocatalysis; photocatalyst; visible-light photocatalysts; membrane separation; organic synthesis; photocatalytic conversion; water treatment; wastewater treatment

# 1. Introduction

The development of advanced green chemical technologies and processes in organic synthesis and environmental conversions has become one of the most important challenges for chemical researchers in the last decades [1,2] and, particularly, for the ones using heterogeneous photocatalysis (HPC). Too much interest is devoted on using the solar source as a non-exhaustible energy and, in this aspect, visible light photocatalysts play a very crucial role.

Many conventional catalytic processes for chemical production usually employ toxic and hazardous substances as catalysts or solvents, thus, they are not very sustainable in terms of resources, environmental impact and energy efficiency [1–4]. The main reason, from a catalytic point of view, that makes photocatalysis sustainable is the photonic activation mode of the photocatalyst instead of the thermal activation typical of traditional industrial processes [5]. Ideal materials for photocatalysis should possess qualities such as high photoactivity towards near UV and visible region of the electromagnetic spectrum, resistance to photocorrosion, inertness, low cost and low environmental toxicity [1–4]. Photocatalytic reactions generally utilize semiconductors to directly absorb photons above their band gap energy and produce carriers consisting of electrons and holes, thus promoting oxidation and reduction reactions [1–4,6]. The produced electron/hole couple can undergo two different fates: (i) the couple can quickly recombine, in the bulk or on the surface of the semiconductor, releasing the accumulated energy as heat or photons; (ii) the couple can migrate to

the surface of the semiconductor where the promoted electron and the hole can, reduce and oxidize the adsorbed substrates, respectively. In order to employ the photogenerated couples, to induce photocatalytic reactions, the electron/hole recombination should be avoided.

The action of ultraviolet (UV), visible (VIS) or infrared (IR) radiation is necessary to obtain the initiation of a chemical reaction catalyzed by a photocatalyst [3,6,7]. The study of the photocatalytic reactions started in 1972 when Fujishima and Honda [8] discovered that UV light induced water cleavage using a  $TiO_2$  photoanode in combination with a Pt counter electrode immersed in an aqueous electrolytic solution. Since then, photocatalysis has attracted significant attention for its promising applications, mainly in the environmental sector, and particularly, in wastewater purification [6,9-13]. In this process high-energy UV-light frequently induces unselective reactions in which organic and inorganic pollutants in liquid phases are totally degraded to innocuous substances. However, in last years there is an increase in the interest of application of photocatalysis in reactions of synthesis such as selective reduction and oxidation, generating less by-production formation, and this can be achieved by using visible light as energy source [14–18]. Indeed, the imminent energy crisis and growing pollution issues, increased the interest in the utilization of renewable energy sources, such as wind or solar light [19]. In particular, solar energy can be used for the photocatalytic degradation of harmful and toxic organic substances performing photoreduction and photooxidation processes. Furthermore, the photocatalytic process can generate renewable and green energy carriers (e.g., H<sub>2</sub> (and O<sub>2</sub>)) from water splitting [6,20–22]; it can help to decrease pollution (e.g., photocatalytic degradation of organic pollutants) [1,11–13,23]; it can provide energy conversion and materials storage (e.g., photocatalytic reduction of CO<sub>2</sub>) [24–31]; and it can synthesize organic substances providing a sustainable pathway for green synthesis [1–4].

Potential advantages that makes HPC a sustainable approach are [1-4,13,32-34]: (i) possibility to carry out reactions under mild conditions such as room temperature and pressure; (ii) use of environmentally friendly and safer catalysts (e.g., TiO<sub>2</sub>) avoiding the use of dangerous heavy metal catalysts; (iii) reducing/avoiding the use of strong chemical oxidant/reducing agents (e.g., the use of mild oxidants such as molecular oxygen); (iv) possibility to convert contaminants to innocuous byproducts; (v) limiting the use of auxiliary additives; (vi) application to a wide range of substrates in liquid, solid, and gaseous phases; (vii) possibility to use renewable solar energy; and (viii) opportunity to couple HPC with other physical and chemical technologies (e.g., membrane separation and membrane reactors, respectively). Coupling HPC and semipermeable membranes gives systems named photocatalytic membrane reactors (PMRs). These represent a very interesting technology because they minimize the environmental and economic impacts obtaining the advantages to perform chemical reactions and separation processes in a single step [1–4,35–37]. The main benefits of using a membrane are: (i) recovery of the catalyst (immobilizing it on/in the membrane or using the membrane to maintain it in suspension), (ii) selective separation of the molecules employed in the reaction limiting the formation of by-products thus enhancing the selectivity. PMRs can be also coupled with various materials such as adsorbents incorporated in membrane, photocatalysts combined with magnetic material or coated on optical fibers, etc. Moreover, one of the main advantages of the employment of solar light in photocatalytic membrane reactors (PMRs), avoiding UV radiation, is the lowest degradation of polymeric membranes elongating their lifetime. In addition, while most photocatalysts can be activated only by ultraviolet light energy, which is only about 5% in the solar spectrum, visible light is 45% and near-infrared (NIR) is 50% of the solar light energy. Thus, in view of efficient solar-energy utilization, efforts to extend the light response from UV to visible light are necessary.

In the present paper a focus on the most recent advances in the use of visible light photocatalysts for carrying out chemical conversions in liquid phases in batch and PMRs are reported. Some applications on the photocatalytic reduction and oxidation of organics, water treatment and degradation of organic pollutants are reported and their perspectives are discussed.

#### 2. Problems of UV-Light Photocatalysts and Requirement for Vis-Light Photocatalysts

Solar-driven photocatalytic reactions are an attractive clean and effective way to convert solar energy to perform chemical reactions [6,38–40]. The entire process of the heterogeneous photocatalysis in liquid phase can be divided in five independent steps: (1) transfer of reagents from the liquid phase to the catalyst surface; (2) adsorption of reactants; (3) reaction in the adsorbed phase; (4) desorption of the products; (5) removal of the products from the interface solid/liquid. Instead, the step (3), which involves the photocatalytic reaction, can be divided in four stages [3]: (a) light absorption followed by the separation of the electron–hole couple; b) adsorption of reagents; (c) redox reaction; (d) desorption of products. The redox reaction happens in the electronic structure of the semiconductor which is characterized by a conduction band (CB) and a valence band (VB) separated by a band gap of energy (EG). When the semiconductor is excited by photons with energy equal to or higher than the band gap energy level ( $hv \ge E_G$ ), electrons receive energy from the photons and are thus promoted from VB to CB. Electrons and holes that migrate to the surface of the semiconductor can, respectively, reduce and oxidize the reactants adsorbed on the semiconductor surface and this depends on the redox potential (or energy level) of the substrate (Figure 1).



Figure 1. Redox reactions involved in semiconductor photocatalysis.

The photocatalyst's ability to carry out a particular reaction depends on the relative position of the energy levels of the catalyst and the substrate. The adsorbed molecule can be reduced if its reduction potential is higher than that of the photoelectrons or it can be oxidized if its potential is lower than that of the photohole. The semiconductor photocatalyst possess intrinsic band structure that determines its electronic transport properties, including its electron energy-level transition [19]. The photoactivity is promoted by the light absorption, redox potential, charge-carrier mobility and can be improved by modifying the band structure [4]. The most widely used semiconductor for photocatalysis is TiO<sub>2</sub> because it shows advantages as: wide availability, low cost, nontoxicity, and long-term stability [32]. Nevertheless, the TiO<sub>2</sub> photocatalyst is photoactive only in the UV range and its activity is strongly influenced by the recombination of photogenerated electrons and holes [1–4,32,41].

Generally, to increase the light absorption response, the main strategy, reported by different authors, is improving the number of light-active sites on the photocatalyst and restricting charge-carrier recombination [19]. The enhancement of light-active sites can be obtained by two methods: (1) design of semiconductors at nanoscale size improving their surface area, (2) increase of highly active facets of the photocatalyst. Charge-carrier separation can be improved by controlling the morphology and the heterostructure construction with suitable band alignment. Moreover, the presence of open pores in some semiconductors can permit the diffusion of the reactants also into the photocatalyst

material. Indeed, by a one-step and template-free process for the synthesis of meso-crystalline TiO<sub>2</sub>, Bian et al. [41] obtained an increased charge-separation efficiency and a large specific surface area, which enhanced the photocatalytic properties in the photocatalytic oxidation of p-chlorophenol (4-CP) and rhodamine B (RhB), as well as the photocatalytic reduction of Cr<sup>6+</sup> in the aqueous phase. Besides, depositing fine noble-metal particles (e.g., Pt, Ag, Au, Pd, and Rh) on the photocatalyst surface is a practical route to enhance charge separation [19]. In this hybrid nanostructure, a Schottky barrier by Fermi level equilibration between the photocatalyst and metal deposits can be established.

# 2.1. Selectivity of Visible Light Photocatalysts

Most semiconductors photocatalysts, can be activated only by ultraviolet light [6], but UV light in the solar spectrum is only about 5%, instead visible light is 45%, and near-infrared (NIR) is 50% of the solar light energy [19]. Thus, for efficient solar-energy utilization, efforts to extend the light response from UV to visible light and to NIR light should be made. Moreover, high-energy UV-light frequently induces an increase of by-products formation due to the excessive energy input in the reacting environment for the higher production of reducing and/or oxidizing agents. This problem can be limited by using visible light as energy source [42–44]. The mechanism of the visible-light response for visible-light active photocatalysts is the same as that for UV-light-active photocatalysts. The only difference is the lower photon energy needed to activate the photocatalytic cycle that probably causes higher selectivity.

For example, the Palmisano group [45–52] performed various photocatalytic oxidations of aromatic alcohols to aldehydes in water making a comparison of selectivity between rutile and anatase TiO<sub>2</sub> nanoparticles prepared in-house under UV light irradiation. They showed results in terms of selectivity of about 45–74% over rutile TiO<sub>2</sub> nanoparticles for the photo-oxidation of 4-substituted aromatic alcohols to the corresponding aldehydes [48], 41% and 62% of selectivity over anatase and rutile TiO<sub>2</sub> nanoparticles for oxidation of 4-methoxybenzyl alcohols, respectively [49,52], and 60% over rutile TiO<sub>2</sub> nanoparticles for oxidation of benzyl alcohols to benzaldehyde [46]. To improve the selectivity to desired products some researchers studied the photocatalytic oxidation under visible light.

For example, Zhang et al. [53] presented a system working under visible light irradiation constituted by a dye-sensitized anatase TiO<sub>2</sub>- TEMPO (2,2,6,6-tetramethylpiperidinyloxyl) nanoparticles which showed selectivity of over 93% for oxidation of a series of aromatic alcohols and of 98% for benzyl alcohols. Similarly, Higashimoto et al. [54] reported high selectivity (>99% for most of the studied aromatic alcohols) for the photocatalytic oxidation of aromatic alcohols to aldehydes under visible-light irradiation over anatase TiO<sub>2</sub> nanoparticles. Li et al. [44] also, reported over 99% selectivity of the partial photocatalytic oxidation of benzyl alcohol over rutile TiO<sub>2</sub> nanorods under visible-light irradiation. These results are better than that reported under UV light irradiation. The nanorods were prepared by a hydrothermal reaction using rutile TiO<sub>2</sub> as a substrate at 150 °C. A tentative reaction mechanism was proposed by the authors (Figure 2): benzyl alcohol was first adsorbed on the surface of rutile TiO<sub>2</sub> to form a complex which could absorb visible-light to generate electrons and holes, then it was oxidized into the benzaldehyde by electrons transfer and holes-attracted release of H atom. In addition, the unidirectional property of nanorods favored the electron transfer and thus the selectivity [44].



**Figure 2.** A tentative schematic illustration for the reaction of selective photocatalytic oxidation of benzyl alcohol into benzaldehyde over rutile TiO<sub>2</sub> nanorods under visible-light irradiation [44].

#### 2.2. Visible-Light-Active Photocatalysts

To expanse the light-harvesting region from UV to visible, obtaining photocatalysts active under visible light, different methods have been used [19]. These ones concern nanocatalysts [55,56], noble metal loading [57–63], ion doping [64,65], dye sensitization [66], fabrication of nanostructured semiconductors for photocatalysis, including nanosheet, nanotube, and nanorod, various fabrication routes for TiO<sub>2</sub> nanotubes such as hydrothermal, anodization, and template methods [67–71] and new materials such as graphene based materials [20,21,66,72]. Indeed, to avoid photogenerated charge-carrier recombination on the photocatalyst, a design and manufacture of suitable heterostructures is very important to enhance the charge carrier separation. Several semiconductor materials possessing visible-light photoactivity have been prepared to utilize more efficiently solar energy, for example, CdS, CdSe, InP, GaZnON, WO<sub>3</sub>, Ag<sub>2</sub>O, Cu<sub>2</sub>O, BiVO<sub>4</sub>, Bi<sub>2</sub>MoO<sub>6</sub>, Bi<sub>2</sub>WO<sub>6</sub>, RbPb<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>, and others [19]. Among them, CdS is one of the most known, with a long research history [42].

In the last years the development of new materials such as graphene and graphene oxide (GO) as photocatalysts is increasing, for their sustainability and flexibility, in the modification and design of the photocatalysts. In addition to these advantages, the photocatalytic activity of GO under visible light can be implemented by the presence of cationic or anionic dyes [66]. Some dyes having visible light sensitivity are used in photocatalytic systems [73]. Under visible light illumination, the excited dyes can inject electrons into the conduction band of semiconductors to initiate the photocatalytic reactions. Lavorato et al. [66], reported the use of [Ru(bipy)<sub>3</sub>]<sup>2+</sup> dye molecules located in the intergallery space of incompletely delaminated GO by a simple cationic exchange at 60 °C obtaining a photocatalyst that was able to produce hydrogen from water/methanol solutions, under laser light at 532 nm and solar simulated light with or without a cut filter to eliminate all UV light. The authors proposed the following photosensitization mechanism: upon light excitation, [Ru(bipy)3]<sup>2+</sup> reaches the triplet excited state, which has an energy of -1.06 eV with respect to the same reference electrode [74]. Consequently, from a thermodynamic point of view, electron injection from the  $[Ru(bipy)_3]^{2+}$ LUMO into the CB of GO will be favorable [66]. Another photocatalyst used to increase the visible light absorption of a photocatalyst mainly active under UV light such as  $TiO_2$  is alizarin red S (ARS). Li et al. [42], reported the selective oxidation of alcohols with atmospheric  $O_2$  by using a visible light LED as irradiation source and 0.67 mol% of ARS anchored onto TiO2 surface as sensitized photocatalyst [75]. Sometimes, the electron transfer, between the photosensitizer/semiconductor and the reactant, can be limited by their oxidation/reduction potential. To limit this problem, it is possible to introduce a co-catalyst (such as an organometallic complex) [2] that acts as electro mediator

between the photosensitizer/semiconductor and the reactant. In particular, Figure 3, Li et al. [42] reported the following advantages to activate a photocatalyst with this approach: (1) easy charge separation process in space; (2) decrease of the energy barrier of reactants by multistep electron-transfer; (3) increase of reactions selectivity with complexes as active sites; and (4) design to apply on specific reactions.



**Figure 3.** Schematic illustration of the strategy of activating reactants or catalyst with a photoexcited electron-transfer process. P = photosensitizer/semiconductor,  $P^* = the excited state of photosensitizer/semiconductor$ , C = catalyst [42].

Noble metals, including Pt, Au, Pd, Rh, Ni, Cu and Ag have been reported to be very effective for enhancement of TiO<sub>2</sub> photocatalytic activity decreasing the possibility of electron-hole recombination and reducing the band gap energy of the photocatalyst, thus shifting the radiation absorption towards higher wavelengths, permitting to use visible light [57]. Recently, the reduction of various organic compounds has been investigated by using visible light TiO2 based semiconductors loaded with Pd nanoparticles (NPs), also in membrane reactors, for acetophenone reduction [57,59]. Noble metals can improve the photocatalytic properties of TiO<sub>2</sub> NPs [6,60,61,76– 79] because they absorb the excited electrons from  $TiO_2$  limiting the recombination of electrons and holes. Moreover, the localized surface plasmon resonance (LSPR) effect of noble metals, which is the collective electron oscillation on the surface of noble metals, contributes to the strong absorption of visible light. In the experiments on photocatalytic water splitting of an alcohol-water solution, Seh et al. [78] reported that, by using Au/TiO<sub>2</sub> as photocatalyst, the amount of hydrogen produced was 138 mL compared with 7 mL obtained by using pure TiO<sub>2</sub> in 3 h. Mendez et al. [60] found that the absorption edge energy of TiO<sub>2</sub> (3.15 eV) changed after 0.5 wt% Au loading (2.98 eV), therefore, the absorption peak was red-shifted and the Au loading improved the absorption of visible light. Moreover, the duration of the plasmon-excited electrons decay of Au/TiO<sub>2</sub> NPs was 1.5 ns better than a few picoseconds of an individual Au NP [61], thanks to the migrations of electrons from the Au NP surface to the TiO<sub>2</sub> NP, extending the decay time and effectively limiting the recombination of electrons-holes in Au NP.

In recent years, the doping of TiO<sub>2</sub> with nitrogen has grown interest due to the photoactivation by solar light [79,80]. Azami et al. [79] reported a preparation of N-doped TiO<sub>2</sub> by mixing urea and TiO<sub>2</sub> powder under microwave irradiation. The presence of nitrogen makes N-doped TiO<sub>2</sub> active under visible light irradiation with reduced band gap to 2.9 eV. It was reported that the N-doped TiO<sub>2</sub> photocatalyst had good photocatalytic activity with complete degradation of Reactive Red 4 after 60 min. Nitrogen has been also used to improve the photocatalytic activity of graphene. Lavorato et al. [20] reported a new preparation of a nitrogen doped graphene photocatalyst obtained by pyrolysis of chitosan at different temperatures. This type of photocatalyst was more active than GO, which showed photocatalytic activity only under UV light. N-doped graphene exhibited high efficiency for the photocatalytic generation of hydrogen from water/methanol mixtures in the absence of Pt or any other metal with similar efficiency using UV or visible-light. Other semiconductors that draw great attention on their utilization as photocatalysts are metalorganic frameworks (MOFs) that consist of metal clusters interconnected with organic linkers (e.g., MOF-5, UiO-66(Zr), ZIF-8, MIL-125(Ti), etc.) [81]. These semiconductors show limited efficiency under solar light illumination because of the lack of visible light response, but their effective use under visible light can be easily achieved by the modification of their organic linkers or metal centers. For example, NH<sub>2</sub>-MIL-125(Ti) (denoted as NH<sub>2</sub>-M125), as the isostructural MOF of MIL-125(Ti), constituted by cyclic Ti<sub>8</sub>O<sub>8</sub>(OH)<sub>4</sub> oxoclusters and 2-aminoterephthalate ligands, shows extended absorption spectra into the visible-light region (around 550 nm) because of its amino functionality moieties.

#### 3. Outline on Applications of Vis-Light Photocatalysts

#### 3.1. Water Splitting

Hydrogen generation by using visible light is very attractive because it allows to convert and store solar energy in a clean and effective way [1,6,20,42,60,66]. Photocatalysis is one of the main approaches to produce hydrogen by utilizing solar energy. As explained in the paragraph 2, different methods have been ideated to improve the visible light activity of photocatalysts. Among them noble metals such as Au, Ag and Pt, which work as co-catalysts, are very effective to enhance the photocatalytic performance of TiO<sub>2</sub> for water splitting. In the following some types of photocatalysts tested in water splitting and some experimental data are discussed. A summary of the photocatalysts and the main results is reported in Table 1.

The overall photocatalytic water splitting process involves two half reactions, an oxygen evolution reaction (OER) and a hydrogen evolution reaction (HER) [82] which compete with their reverse reaction forming again water. At present, many semiconductor materials have been used as photocatalysts in hydrogen evolution reaction. Some semiconductor materials reported by various authors, such as CdS [83], CdSe [84], InNbO<sub>4</sub> [85], BiVO<sub>4</sub> [86], Bi2MOO<sub>6</sub> [87], Bi2WO<sub>6</sub> [88], TaON [89], g-C<sub>3</sub>N<sub>4</sub> [90,91], (Ga1-xZnx)(N1-xOx), ZnS [92], are capable to utilize visible light [93], but some of these photocatalysts can be degraded by the photocorrosion [82,94,95]. In particular, metal sulfides are subject to rapid photocorrosion through the oxidizing holes which convert some of the excitation energy to promote a chemical decomposition of the semiconductor generating sulfur and metal ions. For example, ZnS and CdS nanoparticles (NPs) have poor stability during the photocatalytic process due to photo-corrosion [92,96] despite: i) the superior photocatalytic activity for hydrogen production under visible or solar light, ii) the rapid generation of the electron-hole pairs by photoexcitation, and iii) the highly negative reduction potentials of excited electrons. Instead, other semiconductors, active only under UV light, such as TiO<sub>2</sub> [32] and SrTiO<sub>3</sub> [97], are stable and efficient for hydrogen evolution.

To enhance the application of sunlight irradiation in water splitting reaction, there are various methods that can be adopted such as doping of metal or nonmetal elements or dye sensitization on various semiconductors [1,4,6,42,61,94]. For example, Au is a metal largely used to dope titanium dioxide improving the visible light absorption of the photocatalyst in the visible range. Au/TiO<sub>2</sub> nanoparticles (NPs) showed good performance in photocatalytic hydrogen generation because of the localized surface plasmon resonance (LSPR) effect of Au/TiO<sub>2</sub> NPs [6]. A parameter that plays an important role in the photocatalytic reaction rate of Au/TiO<sub>2</sub> NPs is the light intensity. Very recently, Xing et al. [6] found that the hydrogen production rate has a super-linear dependence on light intensity in the range 0–7 kW/m<sup>2</sup>, and then a sub-linear dependence in the range 7–9 kW/m<sup>2</sup>. Probably Au's LSPR effect plays a key role in the super-linear relationship because at high intensity the faster recombination rate of electrons and holes limits the growth.

Other interesting new materials successfully used for water splitting under visible-solar light are graphene-based materials [20,21,66]. By coupling [Ru(bipy)<sub>3</sub>]<sup>2+</sup> dye molecules and delaminated GO, it can be obtained a photocatalyst that can produce hydrogen from water/methanol solutions, under laser light at 532 nm and solar simulated light with or without a cut filter to eliminate all UV light [66]. Pristine graphene is not suitable for water-splitting, but by doping heteroatoms (e.g., N, P, etc.), gapless metallic graphene can be turned into a semiconductor. Lavorato et al. [21] reported the

possibility of using alginate, a natural polysaccharide from algae, as a simultaneous graphene precursor and a templating agent for ceria nanoparticles for UV-visible light water splitting ( $\lambda > 380$  nm). They prepared a series of materials consisting of highly crystalline ceria nanoparticles embedded on a few-layer graphene matrix. Changing the pyrolysis temperature and the weight percentage of ceria/alginate, the best sample preparation exhibited about 3 times higher photocatalytic activity for water oxidation to oxygen than commercial ceria. In another work Lavorato et al. [20] studied the photocatalytic activity for hydrogen production of N-doped graphene obtained by pyrolysis of a natural biopolymer such as chitosan. The best photocatalyst was obtained by using a pyrolysis temperature of 900 °C. It showed a similar activity under laser light irradiation at 355 and 532 nm and it was also able to generate hydrogen upon simulated sunlight illumination. Nitrogen doping could increase the hole scavenging by electron donors, extending the lifetime of electrons, resulting in high charge extraction and creating efficient photocatalysis. Garcia et al. [98], obtained a photocatalytic activity under visible light by using phosphorus-doped graphene obtained by the pyrolysis of natural alginate that contained H<sub>2</sub>PO<sub>4</sub>- at 900 °C. This material catalyzes the

generation of H<sub>2</sub> from a water/methanol mixture upon irradiation with UV or visible light.

Another method to design photocatalysts active in the visible light is the formation of a heterojunction [99]. This is an interface between unequal band structures with different semiconductors with suitable band gap alignment. The speed of electron transfer is promoted lowering recombination sites of photoexcited charge carriers due to potential gradient of heterojunction between semiconductors. Luo et al., synthesized 2%NiS/20% g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> (2NS/20CN/STO) as photocatalyst to improve the photocatalytic activity of both g-C<sub>3</sub>N<sub>4</sub> and SrTiO<sub>3</sub> semiconductors for H<sub>2</sub> evolution under UV-visible light irradiation [100]. In fact, the band energy levels of g-C<sub>3</sub>N<sub>4</sub> and SrTiO<sub>3</sub> match, for constructing, an efficient heterojunction, which can enable the separation and transfer of photogenerated charge carriers in the organic-inorganic g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> composite because the valence band (VB) of SrTiO<sub>3</sub> is more positive than that of g-C<sub>3</sub>N<sub>4</sub>, while the conductance band (CB) of g-C<sub>3</sub>N<sub>4</sub> is more negative than that of SrTiO<sub>3</sub>. Moreover, both g-C<sub>3</sub>N<sub>4</sub> and SrTiO<sub>3</sub> have efficient thermodynamic potential for hydrogen production from water splitting, because their CB levels are more negative than the hydrogen production level. NiS, which has a small band gap of 0.5 eV, was used as cocatalyst. Heterojunction construction and NiS cocatalyst enhanced the H<sub>2</sub> production rate for the sample 2%NiS/20%g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> 2 (2NS/20CN/STO) due to an effective charge separation via transportation of photogenerated electrons to NiS. The authors reported that this photocatalyst (2NS/20CN/STO) showed a photocatalytic hydrogen production rate of 32.8, 8.9 and 4.2 times the value obtained with pure g-C<sub>3</sub>N<sub>4</sub>, SrTiO<sub>3</sub> and 20%g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> (20CN/STO), respectively.

Recently, Gao et al. [82], studied the possibility of using photocatalytic materials active under UV light to obtain overall water splitting by starting with visible light irradiation. They synthesized the following photocatalysts: Pr<sup>3+</sup>-CaTiO<sub>3</sub> (Pr<sup>3+</sup>-CTO), Pr<sup>3+</sup>-Y<sub>2</sub>SiO<sub>5</sub> (Pr<sup>3+</sup>-YSO) and Pr<sup>3+</sup>-Y<sub>2</sub>SiO<sub>5</sub>/Pr<sup>3+</sup>-CaTiO<sub>3</sub> (Pr<sup>3+</sup>-CTYS). A complex photocatalyst CaTiO<sub>3</sub>/Pr<sup>3+</sup> Y<sub>2</sub>SiO<sub>5</sub>/RGO (reduced graphene oxide) that was able to upconvert visible light into UV light which was then used to excite UV, formed charge pairs by taking advantage of up conversion luminescence properties of Pr<sup>3+</sup>-Y<sub>2</sub>SiO<sub>5</sub> (Pr<sup>3+</sup>-YSO). The RGO greatly facilitated the forward electron transfer from photoexcited Pr<sup>3+</sup>-CTO to Pt co-catalyst and suppressed back electron transfer. Moreover, to avoid hydrogen-oxygen reverse recombination reaction to water formation, the oxygen formed in the reaction mixtures was removed by an artificial gill. The conjectured mechanism of RGO/Pr<sup>3+</sup>-CTYS/Pt for photocatalytic hydrogen evolution is described in Figure 4.



Figure 4. Visible-light-driven overall water splitting over RGO/Pr3+-CTYS/Pt system [82].

Photocatalyst	Main Results	Ref.
Au/TiO2 nanoparticles (NPs)	super-linear dependence on light intensity in the range 0–7 kW/m <sup>2</sup> ,	[6]
	and then a sub-linear dependence in the range $7-9 \text{ kW/m}^2$	
[Ru(bipy)3] <sup>2+</sup> @GO	3290 μmol h <sup>-1</sup> g <sup>-1</sup> of hydrogen production under laser irradiation at	[66]
	532 nm	
N-doped graphene	About 55 µmol after 3 h of visible-light (532 nm) laser irradiation	[20]
phosphorus-doped grapheme	H <sub>2</sub> -generation rate 282 $\mu$ mol h <sup>-1</sup> g <sup>-1</sup> under UV/Vis irradiation using	[98]
(Pt-(P)G-4)	triethanolamine	
2%NiS/20%g-C3N4/SrTiO3	hydrogen production rate of 1722.7 $\mu$ mol h $^{-1}$ g $^{-1}$	[100]
(2NS/20CN/STO)		
CaTiO <sub>3</sub> /Pr <sup>3+</sup> Y <sub>2</sub> SiO <sub>5</sub> /RGO	Up conversion of visible light into UV light	[82]

Table 1. Summary of som	e photocatalyst	ts tested in water	r splitting and	d main results.
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#### 3.2. Photocatalytic Reductions

To develop a sustainable chemistry, the photocatalytic reduction reactions involving various semiconductor materials can proceed under mild conditions using various light sources, including solar energy [101]. We have reviewed the state-of-the-art in heterogeneous photocatalytic systems derived from various semiconductors, their composites, and other materials for the selective reduction of different classes of organic compounds including CO<sub>2</sub>, ketones and nitro compounds.

## 3.2.1. Conversion of CO<sub>2</sub>

CO<sub>2</sub> reduction under visible light can supply sustainable liquid fuels and alleviate global warming. Very recently, various authors reported the CO<sub>2</sub> reduction under visible light [24,27–29,102,103]. In particular CO<sub>2</sub> reduction by water to alcohols is very interesting. Microwave-synthesized carbon-dots (mCD) possess unique hole-accepting nature, prolonging the electron lifetime (t<sub>50%</sub>) of carbon nitride (CN) by six folds, favoring a six-electron product [24]. mCD-decorated CN stably produced stoichiometric oxygen and methanol from water and CO<sub>2</sub> with nearly 100% selectivity to methanol and internal quantum efficiency of 2.1% in the visible region.

In the following some types of photocatalysts tested in CO<sub>2</sub> conversion and some experimental data are discussed. A summary of the photocatalysts and the main results is presented in Table 2.

An interesting CO<sub>2</sub> conversion strategy includes the use of adsorbents to remove harmful heavy metals in polluted water and their conversion into valuable photocatalysts for CO<sub>2</sub> reduction without secondary treatment [25]. Calcium silicate hydrate (CSH) nanosheets, with ultrathin thickness (2.8 nm), ultrahigh surface area (637.2 m<sup>2</sup> g<sup>-1</sup>), and abundant surface hydroxyls, are much favorable for

both heavy metals removal and photocatalysis processes. Chen et al. [25] studied four typical heavy metals including Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup>. For Ni<sup>2+</sup> they observed that it was spontaneously converted into a new semiconductor nickel silicate hydroxide that showed a suitable energy level for reducing CO<sub>2</sub> into CO (CO yield up to  $1.71 \times 10^4$  µmol g<sup>-1</sup> h<sup>-1</sup> with 99.2% selectivity under visible light).

Wang et al. [103] reported an artificial photosynthesis for visible-light-driven CO<sub>2</sub> reduction with H<sub>2</sub>O. They fabricated all-solid-state Z-scheme ternary photocatalysts, consisting of two isolated photochemical systems of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) and three-dimensional ordered macroporous carbon-coated TiO<sub>2</sub> (3DOM-TiO<sub>2</sub>@C) combined with Pt nanoparticles as electron-transfer system (g-C<sub>3</sub>N<sub>4</sub>/Pt/3DOM-TiO<sub>2</sub>@C). Photonic crystal structure and carbon-coated nanolayers of 3DOM-TiO<sub>2</sub>@C support enhanced visible light-harvesting efficiency. The vectorial photoelectron transferring from TiO<sub>2</sub>@C  $\rightarrow$  Pt  $\rightarrow$  g-C<sub>3</sub>N<sub>4</sub> boosts the separation and surface enrichment efficiencies of photogenerated electrons and holes. The results showed high yields of CH<sub>4</sub> and quantum efficiency (6.56 µmol h<sup>-1</sup> for 0.1 g catalyst and 5.67%, respectively) during conversion of CO<sub>2</sub> with H<sub>2</sub>O under visible light.

Cu<sub>2</sub>O photocatalyst represents an outstanding choice to convert the CO<sub>2</sub> molecule into solar fuels [104]. Nevertheless, its capacity to adsorb CO<sub>2</sub> is limited and for this reason Luévano-Hipólito et. al. [104], supported Cu<sub>2</sub>O on activated-dolomite (Cu/DA) for the photocatalytic CO<sub>2</sub> conversion to solar fuels (CH<sub>3</sub>OH and HCOH) under LED-visible light. Pure-Cu<sub>2</sub>O resulted in the highest HCOH production (419 µmol g<sup>-1</sup> h<sup>-1</sup>) with a low amount of CH<sub>3</sub>OH generated (11 µmol g<sup>-1</sup> h<sup>-1</sup>). Instead, in the case of supported Cu<sub>2</sub>O in DA the generation of CH<sub>3</sub>OH (38 µmol g<sup>-1</sup> h<sup>-1</sup>) was favored up to 3.4 times. Adekoy et al. [105] reported that visible light driven photoconversion of CO<sub>2</sub> over Cu-modified TGCN (TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>) composite yielded 2574 mmol g<sup>-1</sup> of CH<sub>3</sub>OH [105,106]. Z-scheme-type photocatalysts with two photochemical systems of graphic-C<sub>3</sub>N<sub>4</sub> (g-C<sub>3</sub>N<sub>4</sub>) and anatase TiO<sub>2</sub> (A-TiO<sub>2</sub>) nanocrystals combined with Au nanoparticles (NPs) [(Au/A-TiO<sub>2</sub>)@g-C<sub>3</sub>N<sub>4</sub>] designed by Wang et al. [107] exhibited excellent photoreduction of CO<sub>2</sub> under visible light irradiation and 37.4 µmol g<sup>-1</sup> h<sup>-1</sup> of CH<sub>4</sub> was produced.

To limit the increased global energy crisis and environmental problems it is important to use renewable materials such as syngas, hydrocarbons, and alcohols. A route for their production is CO<sub>2</sub> photoreduction under visible light [108]. High value-added chemicals in the industry can be obtained by reduction of syngas with different H<sub>2</sub>:CO ratios. Qui et al. [108], proposed a novel route to produce syngas for solar-to-fuel conversion in an artificial photosynthetic system. They carried out interfacial engineering by designing a series of heterostructured layered double-hydroxide/MoS<sub>2</sub> nanocomposites (CoAl-LDH/MoS<sub>2</sub>-x) via electrostatic self-assembly for CO<sub>2</sub> photoreduction. The authors reported that were able to modulate the syngas ratio (H<sub>2</sub>:CO) from 1:1 to 9:1 by visible-light irradiation ( $\lambda > 400$  nm) under the control of the interface-rich heterostructures.

Photocatalyst	Main Results	Ref.
Microwave-synthesized carbon-dots	Carbon dioxide reduction nearly 100% selectivity to	24
(mCD)	methanol by pure water	
Nickel silicate hydroxide	CO yield up to $1.71 \times 10^4 \mu mol  g^{-1}  h^{-1}$ with 99.2% selectivity	25
	under visible light	
g-C3N4/Pt/3DOM-TiO2@C	CH₄ yield of 6.56 µmol h⁻¹ for 0.1 g catalyst and 5.67% of	96
-	quantum efficiency	
Supported Cu <sub>2</sub> O on activated-dolomite	CH3OH generation of 38 µmol g <sup>-1</sup> h <sup>-1</sup>	97
(Cu/DA)		
Cu-modified TGCN (TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> )	CH <sub>3</sub> OH yield of 2574 mmol g <sup>-1</sup>	98
[(Au/A-TiO <sub>2</sub> )@g-C <sub>3</sub> N <sub>4</sub> ]	Formation rates of CH4 is 37.4 µmol g <sup>-1</sup> h <sup>-1</sup>	100
CoAl-LDH/MoS <sub>2</sub> -x	Modulation of the syngas proportion (H2:CO) from 1:1 to	101
	9:1	

Table 2. Summary of some photocatalysts tested in CO2 conversion and main results.

#### 3.2.2. Photocatalytic Hydrogenation of Ketones

The reduction of carbonyl compounds, such as acetophenone (AP), in the corresponding alcohols, such as phenyl ethanol (PE), plays an important role in organic synthesis [57,59,109]. In particular, phenyl ethanol (PE), is a common precursor for the preparation of analgesic and antiinflammatory drugs as well as fragrances and perfumes [57,59,109]. The choice of solvent and electron-hydrogen donor, to achieve the photocatalytic transfer hydrogenation of organic molecules, is essential. In the following some types of photocatalysts tested in ketone hydrogenation and some experimental data are discussed. A summary of the photocatalysts and the main results is reported in Table 3.

Li et al. [42] reported a photocatalytic transfer hydrogenation of carbonyl compounds, under visible light irradiation, by coupling the semiconductor CdS with four types of iridium complexes (Figure 5). The iridium complexes are activated by the photoexcited electron from CdS, and they play dual functions, acting as the acceptor of electron as well as the catalytic sites for organic transformation. The authors reported high selectivity values on visible light photocatalytic hydrogenation of various ketones.



**Figure 5.** Structures of iridium-based complexes and [Cp\*Rh(bpy)(H<sub>2</sub>O)]<sup>2+</sup> used as co-catalysts, (Cp\* is the excited state catalyst- photosensitizer) [42].

Call et al. [110] presented a methodology to reduce aromatic ketones and both aliphatic and aromatic aldehydes using a photocatalytic system consisting of a robust and well-defined aminopyridyl cobalt active complex and [Cu(bathocuproine)(Xantphos)](PF<sub>6</sub>) photoredox catalyst illuminated by visible light with H<sub>2</sub>O and amine (Et<sub>3</sub>N or iPr<sub>2</sub>EtN) as electron donor and the hydride source. Tests were carried out in aqueous mixtures (60–80% water). High selectivity towards the hydrogenation of aryl ketones was observed in the presence of terminal olefins, aliphatic ketones, and alkynes. The catalytic system also showed good selectivity for the reduction of acetophenone in the presence of aliphatic aldehydes.

Kotani et al. [111] reported the extended photocatalytic UV response of TiO<sub>2</sub> towards visible light region by combination of dyes (fluorescein (Fl) and rhodamine B (RhB)) withTiO<sub>2</sub> for the photocatalytic hydrogenation of aromatic ketones with triethylamine as a sacrificial electron donor.

Photocatalyst	Main Results	Ref.	
	Pyruvate TON 790, cyclohexane		
Iridium based complex supported on CdS	carboxaldehyde TON 381, Acetophenone	[42]	
	TON 220		
Aminonuridad scholt complex active and	High selectivity towards the hydrogenation		
[Cu(hathogunraina)/(Yantahog)](PE6) photorodox	of aryl ketones was observed in the presence	[110]	
	of terminal olefins, aliphatic ketones, and	[110]	
Catalyst	alkynes		
DPD TO	Phenylethanol production initial reaction rate	[111]	
KIID-11O2	0.70 mol dm <sup>-3</sup> h <sup>-1</sup>	[111]	
Pd/TiO <sub>2</sub>	Phenylethanol Productivity 22 mg gTiO2 <sup>-1</sup> h <sup>-1</sup>	[57]	
	Phenylethanol Productivity	[50]	
Pa/1102/FAU	99.6 mg gtio2 <sup>-1</sup> h <sup>-1</sup>	[59]	

Table 3. Summary of some photocatalysts tested in ketone hydrogenation and main results.

TON = Turnover Number.

Recently Molinari's group [57,59] synthesized different titanium based photocatalysts for the photocatalytic hydrogenation of acetophenone. Hydrogenation tests were carried out using water as solvent and formic acid as electron hydrogen donor also in a PMR under UV and visible light irradiation (see paragraph 4.2.2). In another work [109] the authors tested the photocatalytic activity of TiO<sub>2</sub> and Pd/TiO<sub>2</sub> for the same photocatalytic reaction under UV light using ethanol as both solvent and hydrogen-electron donor and a water/ethanol solution. By comparing the results obtained in batch [57,109] the authors found that the best solvent for this reaction was ethanol, indeed, the yield obtained using water as solvent with 7.5% of formic acid (1.9 M) was double than that obtained using water/ethanol 50/50, but it was lower than that using pure ethanol. This means that, in perspective to apply the photocatalytic hydrogenation in a membrane reactor, ethanol could not be the best solvent for all type of polymeric membranes.

#### 3.2.3. Photocatalytic Hydrogenation of Nitrocompounds

Nitroaromatic compounds cause severe health hazards to human, animal, and aquatic life because they are dangerous and toxic organic chemicals [112]. The intensively use of these compounds in wars and explosive industrial applications, caused a considerable environmental pollution. For this reason, some researchers are studying the reduction of nitroaromatic compounds to their corresponding aromatic amines [112]. This reaction is even more interesting if it is performed by using ecofriendly alternatives such as photocatalysis under visible light. In the following some types of photocatalysts tested in nitro compounds hydrogenation and some experimental data are discussed. A summary of the photocatalysts and the main results is reported in Table 4.

Recently, the photo-reduction of nitro derivatives was performed by using dye sensitized TiO<sub>2</sub> and transition metal nanoparticles [113]. Various nitrobenzenes were reduced to anilines using Rusensitized TiO<sub>2</sub> photocatalysts by using high power LEDs (Luxeon, 3 W, 530 nm) or sunlight as irradiation source. Gazi et al. [114] reported the study of several dyes with the absorption band in the visible region (e.g., alizarin S red, bromophenol blue, bromopyrogallol red, rhodamine B, methylene blue, rose Bengal and eosin Y) for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by using NaBH<sub>4</sub> as electron donor. The best result in terms of conversion (60% in 50 min) was obtained by using eosin Y on resin (REY) as catalyst.

Graphite-like graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has grown significant interest in the last few years. Kumar et al. [112] reported a simple method for preparing g-C<sub>3</sub>N<sub>4</sub>@ Fe<sub>3</sub>O<sub>4</sub>NPs based on thermal polycondensation of melamine and coprecipitation of ferric and ferrous salts. The obtained material (g-C<sub>3</sub>N<sub>4</sub>@Fe<sub>3</sub>O<sub>4</sub>NPs) had a porous structure, abundant surface functional groups, strong magnetism, electrostatic attraction, and electron donor–acceptor interaction. This photocatalyst offered the efficient adsorption of chromium species in a wide pH range, showing high removal efficiency towards Cr(VI) and Cr(III). In addition, g-C<sub>3</sub>N<sub>4</sub>@Fe<sub>3</sub>O<sub>4</sub>NPs can catalyze the NaBH<sub>4</sub>-mediated reduction of 2-nitroaniline (2-NA) and 4-nitroaniline (4-NA) under the irradiation of visible light with

activity higher than Fe<sub>3</sub>O<sub>4</sub>NPs. Furthermore, the authors reported that this material, through magnetic decantation, can be reused in four successive cycles of 2-NA and 4-NA reduction.

Very recently, Wang et al. [115] reported the hydrogenation of nitrobenzene to produce aniline, azoxybenzene and azobenzene by using CQDs/ZnIn<sub>2</sub>S<sub>4</sub> nanocomposite under visible light. An optimized production of aniline was obtained over 3.0 wt% CQDs/ZnIn<sub>2</sub>S<sub>4</sub> nanocomposite in a reaction medium of TEOA:MeOH (1:1), while a strong alkaline reaction medium promoted N-N coupling to produce azoxybenzene and azobenzene.

Table 4. Summary of some photocatalysts tested in nitro compounds hydrogenation and main results.

Photocatalyst	Main Results	Ref.
Eosin Y on resin (REY)	4-Nitrophenol (4-NP) conversion 60% in 50 min.	[114]
g-C3N4@ Fe3O4NPs	Visible light activity higher than Fe <sub>3</sub> O <sub>4</sub> NPs	[112]
3.0 wt% CQDs/ZnIn <sub>2</sub> S <sub>4</sub>	Full conversion of nitrobenzene after irradiation for 16 h	[115]

#### 3.3. Total and Partial Oxidations

The selective oxidation is one of the major transformations in organic chemistry. Photocatalytic oxidation of organic compounds by solar light is a promising strategy for environmentally benign conversion processes [116]. In the last years the possibility of using cheap and eco-friendly processes, compared to the utilize of strong oxidants which generate toxic wastes, has become imperative. For this reason, interest is growing to perform these reactions by photocatalytic mode.

#### 3.3.1. Oxidation of Primary and Secondary Alcohols to Aldehydes and Ketones

There are many studies on this research subject but here only some very recent articles are reported on the photocatalytic oxidation of organic compounds under visible light [116–122]. Gogoi et al. [116] tested the photocatalytic activity of TiO<sub>2</sub> and Au-TiO<sub>2</sub> for oxidation of primary and secondary alcohols to aldehydes and ketones under visible light irradiation. As expected, Au-TiO<sub>2</sub> was found to be more efficient than TiO<sub>2</sub> alone. In the following some types of photocatalysts tested in the oxidation of primary and secondary alcohols and some experimental data are discussed. A summary of the photocatalysts and the main results is reported in Table 5.

Lv et al. [117] studied a new type of photocatalyst, (Pd/(NH<sub>4</sub>)<sub>x</sub>WO<sub>3</sub>/WO<sub>3</sub>, working under visible light irradiation, that exhibited higher selectivity in comparison to Pd/WO<sub>3</sub> nanorods in the partial conversion of aqueous benzyl alcohol into benzaldehyde (80% selectivity for benzaldehyde production with ca. 84% conversion of benzyl alcohol).

Photocatalytic alcohol oxidation can improve green fuels synthesis applications such as hydrogen production [118]. A new Z-scheme catalyst was constructed for this purpose: ZnIn<sub>2</sub>S<sub>4</sub> nanosheets were grown on the surface of CeO<sub>2</sub> nanorods. This 2D/1D composite can form solid Z-scheme heterostructures that combines the outstanding visible-light absorption of ZnIn<sub>2</sub>S<sub>4</sub> nanosheets, and the fast charge transport of CeO<sub>2</sub> nanorods, with an improved photocatalytic efficiency. The benzaldehyde and hydrogen yields obtained were 664.1 and 1496.6  $\mu$ mol gcat<sup>-1</sup> h<sup>-1</sup>, respectively.

Guo et al. reported a good oxidation efficiency and selectivity towards the conversion of benzyl alcohol into benzaldehyde under visible-light irradiation by using a series of novel Z-scheme BiFeO<sub>3</sub>-(carbon nanotubes (CNTs)-polypyrrole(PPy) prepared via hydrothermal reaction and oxidative polymerization [119]. This photocatalyst presented a benzyl alcohol conversion rate and selectivity to benzaldehyde of about 83.2% and 99.3%, respectively.

Verma et al. [120] tested three different catalysts based on TiO<sub>2</sub> doped with Au: Au/TiO<sub>2</sub> nanotube, Au/TiO<sub>2</sub> nanorod and Au/TiO<sub>2</sub> microporous. The results, obtained carrying out the reaction with thermal activation conditions in dark, were compared with those performed under visible light irradiation ( $\lambda > 420$  nm) at 373 K. The most active photocatalyst, under the same reaction conditions, was found to be Au/TiO<sub>2</sub> nanorod. It showed a performance of 33% yield with the thermal activation in dark and 55% yield of benzaldehyde with an external quantum efficiency of 3.4% under

visible light irradiation ( $\lambda \ge 420$  nm) at 373 K for 4 h. The enhanced catalytic performance was attributed to the Au-LSPR phenomenon.

Photocatalyst	Main Results	Ref.
Au-TiO <sub>2</sub>	Au-TiO2 higher photocatalytic activity than TiO2	[116]
Pd/(NH4)xWO3/WO3	80% selectivity for benzaldehyde production with ca. 84% conversion of	[117]
	benzyl alcohol.	
CeO <sub>2</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	The benzaldehyde and hydrogen yields obtained were 664.1 and 1496.6 $\mu$ mol	[118]
	gcat <sup>-1</sup> h <sup>-1</sup> , respectively.	
BiFeO <sub>3</sub> -(CNTs)	Benzyl alcohol conversion rate and selectivity to benzaldehyde of about	[119]
(PPy)	83.2% and 99.3%, respectively.	
Au/TiO2 nanorod	55% yield of benzaldehyde with an external quantum efficiency of 3.4%	[120]
g-C3N4/TiO2	turnover frequency (TOF) of over 550 h <sup>-1</sup>	[121]
S-doped g-C <sub>3</sub> N <sub>4</sub>	H2 production rate 13.2 times higher than bulk g-C3N4, H2 and benzaldehyde	[122]
	production rate of 3.76 and 3.87 $\mu$ mol h <sup>-1</sup> , respectively.	

Table 5. Summary of some photocatalysts tested in oxidation of alcohols and main results.

Recently, significant progresses have been made in the photocatalytic activity of graphiticcarbon nitride (g-C<sub>3</sub>N<sub>4</sub>) [121]. Mohammadi et al. [121] synthesized spray-dried g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> granules, through a pyrolysis process of urea and TiCl<sub>4</sub> as the precursors. g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>, and spray-dried g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> granules (TCNg) were used for the photocatalytic oxidation of benzyl alcohol (BA) to benzaldehyde (BAL) in a batch reactor under visible light irradiation. The results showed that TCNg, was more active on the photocatalytic oxidation of benzyl alcohol with an average turnover frequency (TOF) of over 550 h<sup>-1</sup>.

Zhang et al. [122] proposed an interesting utilization of solar energy by coupling H<sub>2</sub> generation and selective oxidation of benzyl alcohol. They synthesized heteroatom doped g-C<sub>3</sub>N<sub>4</sub> hierarchical mesoporous spheres. S-doped g-C<sub>3</sub>N<sub>4</sub> showed 13.2 times higher H<sub>2</sub> production rate than bulk g-C<sub>3</sub>N<sub>4</sub> under visible-light. Having the photocatalyst a dual function, as H<sub>2</sub> production and selective oxidation of benzyl alcohol, it exhibited outstanding activity with a H<sub>2</sub> and benzaldehyde production rate of 3.76 and 3.87 µmol h<sup>-1</sup>, respectively.

#### 3.3.2. Partial Oxidation of Alkanes and Alkenes: Oxidation of Cyclohexane

Selective activation of C (sp<sup>3</sup>) and H bonds can be used to develop new strategies to produce high-value organic molecules for their use in the chemical, pharmaceutical and agricultural, industries [123]. An interesting photocatalytic reaction of green chemistry is the cyclohexane oxidation to cyclohexanol (A) and cyclohexanone (K) (the mixture of both is called KA oil) with the use of clean and low-cost molecular oxygen as the oxidant and solar light as the driving force [123–125]. The obtained products are important intermediates to fabricate nylon-6 and nylon-66. In the following some types of photocatalysts tested in the partial oxidation of alkanes and alkenes and some experimental data are discussed. A summary of the photocatalysts and the main results is reported in Table 6.

Cyclohexanol and cyclohexanone can be produced from cyclohexane in the liquid phase using titanium dioxide under mild conditions [126,127]. However, the bandgap of titanium dioxide (3.2 eV) implies the absorption of photons with wavelengths below 387 nm to promote photoelectrons from the valence band to the conduction band. To extend the absorption spectra of TiO<sub>2</sub> to the visible light region limiting recombination of photoelectrons and photoholes, Zhao et al. [81], synthesized a new photocatalyst named NH<sub>2</sub>-MIL-125(Ti)/TiO<sub>2</sub> obtained by coupling metal organic frameworks MOFs (see Section 2) and TiO<sub>2</sub>. Despite, the bandgap obtained for this photocatalyst was 2.70 eV, which meant wavelengths lower than 460 nm, the authors reported an enhancement of the photocatalytic performance of NH<sub>2</sub>-MIL-125(Ti)/TiO<sub>2</sub> three times higher than that of NH<sub>2</sub>-MIL-125(Ti) under visible light ( $\lambda > 420$  nm) for the photocatalyst based on MOFs (MoS<sub>2</sub>@Cu/Cu<sub>2</sub>O@C) was reported to be active under visible light ( $\lambda > 420$  nm) for cyclohexane oxidation. Peng et al. [128], reported the

synthesis of this new composite photocatalyst prepared by immersing the guest (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> (ammonium tetrathiomolybdate) into Cu-metal–organic framework (MOF) polyhedra host and subsequently pyrolyzing the Cu-MOF–guest polyhedra to encapsulate MoS<sub>2</sub> into Cu/Cu<sub>2</sub>O@C. This photocatalyst showed higher photocatalytic cyclohexane oxidation performance compared to the pristine MoS<sub>2</sub> or Cu/Cu<sub>2</sub>O@C. This behaviour is probably due to its heterojunction band reconstruction and to the presence of Cu nanoparticles that capture electrons and prevents electron–hole recombination. Other types of semiconductors that show photocatalytic activity under visible light are bismuth oxyhalides (BiOX, X=Cl, Br, I) because they have adequate chemical stability and desirable electrical and optical properties [129,130].

**Table 6.** Summary of some photocatalysts tested in partial oxidation of alkanes and alkenes and main results.

Photocatalyst	Main Results	Ref.
NH2MIL-125 TiO2	Photocatalytic activity three times higher than that of NH2-MIL-125(Ti)	[81]
MoS2@Cu/Cu2O@C	Conversion of 1.31%, selectivity to cyclohexanol and to cyclohexanone of 59	[128]
	and 39%, respectively	
BiOI	Conversion and selectivity of cyclohexane to cyclohexanol 0.0011% and over	[123]
	80%, respectively	
NH2MIL-125 TiO2 MoS2@Cu/Cu2O@C BiOI	Photocatalytic activity three times higher than that of NH2-MIL-125(Ti) Conversion of 1.31%, selectivity to cyclohexanol and to cyclohexanone of 59 and 39%, respectively Conversion and selectivity of cyclohexane to cyclohexanol 0.0011% and over 80%, respectively	[81] [128 [123

Among the bismuth oxyhalides, bismuth oxyiodide (BiOI), which is stable in water and has low toxicity, exhibits the narrowest bandgap (1.8–1.9 eV) and highest photocatalytic performance within the visible light region [131]. Contreras et al. [123], studied different samples of bismuth oxyiodide and they reported that all BiOI photocatalysts showed higher selectivity for cyclohexanol than cyclohexanone.

#### 3.3.3. Photocatalytic Production of Vanillin

Vanillin (4-hydroxy-3-methoxybenzaldehyde, CsHsO<sub>3</sub>) is a biophenol relatively abundant (in the form of a  $\beta$ -D-glucoside) in the green pods of the orchid *Vanilla planifolia* which was isolated for the first time by Gobley in 1858 [132]. This substance has many applications in food, perfume and pharmaceutical industries [17,132]. Only 1% is obtained by extraction from the plant *Vanilla planifolia* which requires a very long and expensive process to obtain the "natural" product. The remaining 99% is produced by chemical syntheses which allow one to obtain a product almost 100 times cheaper than the natural one [133–135]. An attractive and alternative synthesis to the biotechnological and chemical processes for the aromatic aldehydes may be the photocatalysis at room temperature and atmospheric pressure, even more if it can be conducted under visible light [136,137]. In the following some types of photocatalysts tested in the photocatalysts and the main results is reported. in Table 7.

Parrino et al. studied the photocatalytic oxidation of *trans*-ferulic acid to vanillin (FA, C<sub>10</sub>H<sub>10</sub>O<sub>4</sub>) in aqueous solution under visible light by using different commercial and home-prepared TiO<sub>2</sub> [138]. The main product was CO<sub>2</sub>, whereas secondary oxidation products were organic species such as vanillin, caffeic acid, homovanillic acid, and vanillylmandelic acid. Among different alternative sources to produce vanillin, the valorization of renewable lignocellulosic biomass can be considered as interesting step towards sustainability [139]. For this purpose, lignin, an aromatic amorphous polymeric material, can be used as a starting material for the production of vanillin. The oxidative depolymerization can allow the conversion of lignin to small phenolic compounds such as vanillin, syringaldehyde and *p*-hydroxybenzaldehyde [134,135]. Vanillyl alcohol (VAL) is considered a lignin model substrate that can be converted selectively into vanillin.

Al-Hunaiti et al., synthesized NPs using a route phytomediated by *Boswellia carterii* extract [139]. The spinel ZnFe<sub>2</sub>O<sub>4</sub> with a relatively narrow band gap of about 1.9 eV had visible-light response, good photochemical stability and low cost. The authors reported that ZnFe<sub>2</sub>O<sub>4</sub> showed selectivity to vanillin up to 99% at a conversion over 98% and turn-over frequency values up to 1600 h<sup>-1</sup> in the

presence of H<sub>2</sub>O<sub>2</sub> and base. Furthermore, ZnFe<sub>2</sub>O<sub>4</sub> particles are magnetic semiconductor materials [140] and can be magnetically separated, after the photocatalytic reaction, from the suspension system thanks to their magnetic properties.

Photocatalyst	Main Results	Ref.
ZnFe <sub>2</sub> O <sub>4</sub>	Selectivity to vanillin up to 99% at a conversion over 98% and turn-over frequency	[139]
	values up to 1600 h <sup>-1</sup> in the presence of H2O2 and base	
1Ce/TiO2-BS	Maximum conversion of 39.7% with selectivity values of 99% towards vanillin	[141]
5Zr/TiO2-BS	Maximum conversion of 52.4% with selectivity values of 99% towards vanillin	[141]

Table 7. Summary of some photocatalysts tested in vanillin production and main results.

Vanillin can be produced also by photooxidation of vanillyl alcohol. Very recently Martin-Perales [141] et al. studied this synthesis by using TiO<sub>2</sub>-based materials as photocatalysts [141]. The absorption of visible light, together with the electronic properties and with the photocatalytic efficiency of the synthesized titania, was improved by incorporation of Ce and Zr oxides on the titania surface in comparison to pure TiO<sub>2</sub>. The best catalytic behavior was obtained for 1Ce/TiO<sub>2</sub>-BS and 5Zr/TiO<sub>2</sub>-BS samples, with a maximum conversion of 39.7% and 52.4% for ceria and zirconia modified samples, respectively, and selectivity values of 99% towards vanillin and carbon balance higher than 98%.

## 3.3.4. Benzene Oxidation to Phenol

Another important oxidation reaction widely studied is the direct benzene oxidation to phenol [142–152]. Phenol is an important chemical intermediate for the synthesis of petrochemicals, agrochemicals, and plastics [1–4]. The choice of a suitable photocatalyst is especially important to control the reaction progress and increase the phenol selectivity [145]. So far, several studies were reported on the visible light-induced catalytic oxidation reaction of benzene to phenol in the presence of hydrogen peroxide [145,148–152]. In the following some types of photocatalysts tested in the benzene oxidation to phenol and some experimental data are discussed. A summary of the photocatalysts and the main results are reported in Table 8.

Photocatalyst	Main Results	Ref.
[RuII(Me2phen)3] <sup>2+</sup> and [CoIII(Cp*)(bpy)(H2O)] <sup>2+</sup>	Yield of phenol about 30% and quantum yield (QY) 1.7%	[145]
Pt-WO <sub>3</sub>	Selective hydroxylation of benzene to phenol $300 < \lambda < 500 \text{ nm}$	[150]
Pt-WO <sub>3</sub>	Selectivity of phenol over 70% $420 < \lambda < 540 \text{ nm}$	[149]
10 wt% Fe-modified g-C <sub>3</sub> N <sub>4</sub>	Phenol yield 4.8% and phenol selectivity 3.2%	[151]
Au-Pd/g-C <sub>3</sub> N <sub>4</sub>	Benzene conversion 26% and phenol selectivity 100%	[152]

Table 8. Summary of some photocatalysts tested in benzene oxidation to phenol and main results.

Han et al. [145] reported the photocatalytic hydroxylation of benzene to phenol in a O<sub>2</sub>-saturated acetonitrile solution containing [RuII(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+</sup> as a photocatalyst, [CoIII(Cp<sup>\*</sup>)(bpy)(H<sub>2</sub>O)]<sup>2+</sup> as an efficient photo-catalyst activator for both the water oxidation and benzene hydroxylation reactions, and water as an electron source in the presence of Sc(NO<sub>3</sub>)<sub>3</sub>. During the photocatalytic oxidation of benzene by O<sub>2</sub> the yield of PhOH remained constant while increased the by-product formation (p-benzoquinone) caused by further oxidation of phenol in the reaction environment. The TON for the production of both phenol and benzoquinone was determined to be 500 (where the TON of p-benzoquinone is counted three times). By increasing the concentration of the catalyst and decreasing the concentration of the benzene substrate, it was obtained a yield of phenol based on benzene of about 30%. The quantum yield (QY) was determined to be 1.7% from the amount of PhOH produced during the photocatalytic reaction under photoirradiation ( $\lambda = 440$  nm) for 1 h.

Tungsten trioxide (WO<sub>3</sub>) is one of the promising visible-light photocatalysts having a direct band-gap excitation at ca. 2.7 eV. Tomita et al. [150], reported that the Pt-deposited WO<sub>3</sub> (Pt-WO<sub>3</sub>) photocatalyst exhibited selective hydroxylation of benzene to phenol in the presence of O<sub>2</sub> and H<sub>2</sub>O under light irradiation of both UV light and visible light ( $300 < \lambda < 500$  nm). Instead, Kurikawa et al. [149], focused on understanding the photocatalytic activities for hydroxylation of benzene on the Pt-WO<sub>3</sub> photocatalyst under irradiation of only visible light ( $420 < \lambda < 540$  nm).

Another photocatalyst with absorption setting at wavelengths of 460 nm is g-C<sub>3</sub>N<sub>4</sub>. Chen et al. [151] reported that its absorption is extendable to ~650 nm by iron complexation. The authors reported that Fe-g-C<sub>3</sub>N<sub>4</sub> was able to oxidize directly benzene to phenol using hydrogen peroxide. With 10 wt% Fe-modified g-C<sub>3</sub>N<sub>4</sub> catalysts, the phenol yield based on benzene was 1.8% in the dark and 4.8% in visible light. However, the phenol selectivity based on H<sub>2</sub>O<sub>2</sub> was 3.2% in the dark and 8.3% under visible light.

Under optimized conditions, a mesoporous photocatalyst based on Au–Pd nanoparticles incorporated into g-C<sub>3</sub>N<sub>4</sub> showed benzene conversion of 26% at a phenol selectivity of 100%, giving no dihydroxylated by-products [152]. This photocatalyst was prepared by a coassembly method using melamine as the carbon and nitrogen source, polyvinyl pyrrolidone as the dispersing agent, and pulse laser ablation in liquid technique for preparing gold nanoparticles and subsequent decoration with Pd nanoparticles. At the final stage, Au–Pd/g-C<sub>3</sub>N<sub>4</sub> nano-photocatalyst was obtained via low-ramping pyrolysis in an argon atmosphere.

#### 3.3.5. Water Treatment

The growing increase of pharmaceutical and agricultural pesticide products as environmental pollutants require an enhancement of wastewater treatment to limit potential risks to aquatic organisms and human health [1,153]. Photocatalysis has emerged as a foremost reliable application with high efficiency for organic pollutants degradation due to its benefits of good photocatalytic activity, nontoxicity, chemical inertness, and low cost [1,153–156]. Pesticides are the most harmful for humans and environment among various organic pollutants [157]. Currently, the conventional methods used for pesticide removal are membrane separation, surface adsorption, biodegradation, and photocatalytic degradation. The most studied photocatalyst for the degradation of a wide range of dyes, pharmaceuticals, and organic compounds is TiO<sub>2</sub> [158] but, also ZnO has received much attention by some authors [159]. The major influential parameters for the efficient degradation of organic contaminants are the structural and surface characteristic of semiconducting materials such as surface area, average particle size, crystalline structure, bandgap, porosity and surface density [160]. The surface of most of the metal oxides such as ZnO, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> is also a good adsorbent of organic contaminants in addition to the photocatalytic property. In the following some types of photocatalysts tested in water treatment and some experimental data are discussed. A summary of the photocatalysts and the main results is reported in Table 9.

Premalatha and Miranda [161] studied the degradation of  $\lambda$ -cyhalothrin (L-CHT) under visible light by using ZnO–Bi<sub>2</sub>O<sub>3</sub> as photocatalyst. The results showed that, compared to pristine ZnO, a degradation percentage of 85.7% was achieved within 120 min of the photocatalytic process.

Thi et al. [162] studied the photocatalytic degradation of monocrotophos pesticide (MCP) under visible radiation by using ZnO doped with Cu that prevented the recombination of photo-excited e– and h+ of ZnO. The synthesized photocatalyst showed photocatalytic activity for the degradation of MCP under visible radiation.

The photocatalytic abilities of the introduction of ions Fe, Gd, and N on TiO<sub>2</sub> for the degradation of methylene blue (MB) under visible light were evaluated by Li et al. [163]. The introduction of ions Fe, Gd, and N reduced the particle size of doped TiO<sub>2</sub> and enhanced its surface area and pore volume. The impurity energy levels formed by N and Fe<sup>3+</sup> doping, extended the absorption of TiO<sub>2</sub> into the visible light region, resulting in the reduction of the bandgap. Doping with N and Gd<sup>3+</sup> ions resulted in the formation of defect sites and oxygen vacancies in the TiO<sub>2</sub> lattice. The authors tested a series of Gd–Fe–N–TiO<sub>2</sub> samples synthesized by changing the dosage of gadolinium nitrate at 1, 1.5, 2, 2.5, 3, and 3.5 wt%, further named as G<sub>1.0</sub>FNTO, G<sub>1.5</sub>FNTO, G<sub>2.0</sub>FNTO, G<sub>2.5</sub>FNTO, G<sub>3.0</sub>FNTO, and G<sub>3.5</sub>FNTO.

The co-doped TiO<sub>2</sub> sample showed the best photocatalytic activity when the doped amount of Gd reached 2 wt% (G<sub>2.0</sub>FNTO). The first-order reaction constant of MB photodegradation was 1.10  $h^{-1}$ , which was ten times higher than that of un-doped TiO<sub>2</sub>.

Very recently Mandal et al., studied the degradation of some dyes by using Graphene quantum dots (GQDs) as photocatalyst synthesized from pyrocatechol with a homogenous spherical shape at a size of ~ 8 nm. The results showed that methyl orange was degraded by 52% while methylene blue was degraded by 79.4%, both within two hours [164]. Another problem, in many types of wastewaters, is metals removal and this can be accomplished with transformations using visible light photocatalysts [165]. As an example, hexavalent chromium (Cr(VI)) reduction to Cr(III) has been attracted an extensive attention to limit its concentration in drinking water because the toxicity of Cr(III) is 2–3 orders of magnitude lower than that of Cr(VI). The tanning process usually uses a large quantity of sodium formate, which results in production of end-of-pipe wastewater containing highconcentration hexavalent chromium (Cr(VI)) and formate [165,166]. However, the maximum tolerable concentration of Cr(VI) is 0.05 mg/L in drinking water and 0.5 mg/L in industrial effluents [167]. In addition, the high mobility of Cr(VI) makes it quite easier to pollute both surface water and groundwater [168]. To remove oxidative pollutants in water, the advanced reduction process (ARP) has drawn an increasing interest, even more if this reduction can be obtained by using CO<sub>2</sub>-produced from formate originally existing in wastewater. Liu et al. [165] demonstrated the possibility of in-situ reduction of Cr(VI) by using CO<sub>2</sub> with black TiO<sub>2</sub> photocatalyst under visible-light. The prepared black TiO<sub>2</sub> with nanotube structure enhanced the reduction rate of Cr(VI) as high as 96.2% in the presence of formate. The formate, the black TiO<sub>2</sub> concentration and the pH influenced the Cr(VI) reduction rate.

Photocatalyst	Main Results	Ref.
ZnO-Bi <sub>2</sub> O <sub>3</sub>	Lambda-Cyhalothrin (L-CHT) degradation percentage 85.7%	[161]
	achieved within 120 min	
Cu-ZnO	MCP removal efficiency about 90%	[162]
G2.0FNTO	MB removal amount about 97%	[163]
GQDs	Methyl Orange degraded to 52% while Methylene Blue degraded 79.4%	[164]
	both within two hours	
Black TiO <sub>2</sub>	Reduction rate of Cr(VI) 96.2%	[165]

Table 9. Summary of some photocatalysts tested in water treatment and main results.

# 4. Analysis of Vis-Light Photocatalysts and Types of Conversion of Interest in Photocatalytic Membrane Reactors (PMRs)

There is growing concern for the development of efficient PMRs using renewable and sustainable energy sources, such as solar irradiation [1–4]. Moreover, the use of visible light in photocatalysis allows the use of renewable solar energy, which is an important feature in terms of global sustainability [9,14]. Furthermore, photocatalysis can be combined with other physical and chemical technologies such as membrane separations and membrane reactors [1–4,15,169,170]. The advantage of coupling the visible light activity of the photocatalyst and the separation process in a single unit is mainly the possibility of employment of solar light avoiding UV radiation, thus elongating lifetime of polymeric membranes owing to their lower degradation [57,59].

The conversions using vis-light photocatalysts, described in the previous Sec. 3, can be deeply studied and, eventually, can be carried out in PMRs to take advantage of their peculiar characteristics. In the following paragraphs, some transformations already present in literature using PMRs working under visible-light are reported describing also the main advantages of the membrane role.

#### 4.1. Water Splitting in PMRs

Several reactors have been proposed for solar photocatalytic hydrogen production including the parabolic trough concentrator (PTC), column reactor, compound parabolic concentrator (CPC), surface uniform concentrator (SUC), membrane reactor etc. [171]. In the case of membrane reactors,

some materials, used in ultrafiltration or microfiltration membranes, are hydrophobic such as polypropylene, polyvinylidene fluoride, or polytetrafluoroethylene (PTFE) [172]. These materials are prone to fouling and, in particular, to biofouling, because they are highly hydrophobic and thus, do not meet the fouling resistance criteria. Membrane fouling generally occurs in forms of foulant adhesion/deposition and thermodynamic filtration resistance of gel/cake layer. The accumulation of foulants on the membrane surface can block membrane pores resulting in a low flux through the membrane and a decrease of the membrane life, which means, consequently, an increase of the cost of membrane technology. Therefore, the interest to fabricate membranes with ability to degrade foulants is constantly increasing [173]. Another application of photocatalysis is pre-treatment prior to membrane filtration to eliminate bacteria from the feed solution for biofouling reduction. Lin et al. [172], reported a study on S-doped g-C<sub>3</sub>N<sub>4</sub> nanosheet as a photocatalyst to be used for both water splitting and biofouling reduction. The photocatalytic activity in the generation of H<sub>2</sub> and O<sub>2</sub> was examined in the combination of Ru/SrTiO3:Rh with the addition of [Co(bpy)3]<sup>3+/2+</sup> as electron mediator to improve the charge transfer in a Z-scheme system. The  $H_2$  and  $O_2$  evolution rates in the system were 24.6 and 14.5 µmol<sup>-1</sup>h<sup>-1</sup>, respectively. In addition, S-doped g-C<sub>3</sub>N<sub>4</sub> was incubated with a solution of Escherichia coli to determine its antibacterial effect. This test revealed that S-doped g-C<sub>3</sub>N<sub>4</sub> has a high activity in reducing biofouling on a membrane.

Moreover, the possibility of producing hydrogen from organic matter contained in wastewater by photocatalysis with solar energy is a very attractive way. Rodriguez et al. [174] studied a system combining a photoreactor for hydrogen production by photocatalytic methanol dehydrogenation and a proton exchange membrane fuel cell (PEMFC) obtaining a system to directly convert solar irradiance into electricity. The photocatalytic system consisted of four photoreactors and an aluminum reflector (Figure 6) that was used to optimize irradiation of the slurry with solar light and it was continuously oriented to the sun. Photoreactors were linked in parallel with a recirculating pump and shared their gas phase. The system was purged with helium at 20 mL min<sup>-1</sup> for thirty minutes before each experiment to remove air/O<sub>2</sub> from the photoreactor and the hydrogen stream. The fuel cell contained a 25 cm<sup>2</sup> active area of a membrane separating two compartments: one filled at the anode by photocatalytic hydrogen and the other at the cathode filled by oxygen from the air in a self-breathing mode. Fuel cell performance was followed at constant voltage. Without any purification of hydrogen and without any optimization of the design, the system successfully provided an electric power density of 1 mW cm<sup>-2</sup> of photoreactor optical surface area exposed to the sunlight.



**Figure 6.** Experimental setup for solar conversion into electricity using four photoreactors and an airbreathing PEM fuel cell [174].

#### 4.2. Reductions in PMRs

To our knowledge very few syntheses on reduction reactions in liquid phase in PMR under visible light irradiation are present in scientific literature. In the following some reduction reactions are described. Only in the case of CO<sub>2</sub> conversion many papers are present in literature but here only the very recent ones are reported, more references and details can be found elsewhere [1–4].

#### 4.2.1. CO<sub>2</sub> Conversion in PMRs

In the lasts years the global energy demand of CO<sub>2</sub> conversion into desirable and sustainable solar fuels, such as methanol (CH<sub>3</sub>OH), methane (CH<sub>4</sub>), and formic acid (HCOOH) is increasing [1]. Recently, some works are reported on the use of solar energy in PMRs [175–179].

An interesting natural material that can be used to synthesize membranes is a biopolymer such as chitosan, because of the abundant presence of amine and carboxyl groups, which are favorable for CO<sub>2</sub> adsorption. Zhao et al. [175] prepared and tested chitosan in the photocatalytic conversion of CO<sub>2</sub>, under visible light irradiation. The membrane matrix was: CdS/NH<sub>2</sub>-UiO-66 hybrid membrane where UiO-66 is a metal–organic framework (MOF) with a very high surface area as well as high thermal stability. By incorporating MOFs and semiconductors into membranes, the synergistic activity accelerated the electrons transfer limiting the recombination of electron–hole pairs in the hybrid membrane resulting in an improvement of the CO<sub>2</sub> photocatalytic reduction reaction.

Very recently, Pomilla et al. [176], studied the CO<sub>2</sub> conversion into liquid fuels such as methanol and ethanol by using a catalytic membrane. The photocatalytic membrane (exfoliated C<sub>3</sub>N<sub>4</sub> incorporated into a Nafion matrix) was used in a continuous photocatalytic reactor by using H<sub>2</sub>O as reducing agent. The photocatalytic tests were conducted by irradiating the membrane with both UV and visible light in the range from 360 nm to 600 nm. The authors reported that alcohol production was promoted by the low contact time obtained thanks to the fast removal of the reaction mixture from the reacting volume, which permeated through the membrane, thus limiting the oxidation and/or secondary reactions.

Some authors reported that photocatalytic conversion of CO<sub>2</sub> with H<sub>2</sub>O should promote the reduction of CO<sub>2</sub> by the photogenerated electrons and protons and simultaneous oxidation of H<sub>2</sub>O by the photogenerated holes [177]. These simultaneous reactions are difficult for most of the reported photocatalysts and they need the presence of organic hole scavengers (e.g., triethylamine (TEA),

trimethylamine (TMA), or ethylenediaminetetraacetic acid (EDTA)) [178,179]. To limit this problem, Wang et al. [177], reported the preparation of Cu<sub>2</sub>O–Pt/SiC/IrOx hybrid photocatalyst, composed by a photo-oxidation unit (IrOx) and a photoreduction unit (Cu<sub>2</sub>O–Pt) on SiC surface. This photocatalyst can increase the photocatalytic efficiency by improving the CO<sub>2</sub> adsorption and the lifetime of photogenerated charges. Additionally, to facilitate H<sub>2</sub>O oxidation half reaction and to eliminate the backward reaction of the products, the authors performed this photocatalytic reduction in a spatially separated reaction system consisting of two reaction chambers divided by a Nafion membrane that allowed Fe<sup>2+</sup> and Fe<sup>3+</sup> ions to permeate through (Figure 7). The first chamber was loaded with the Cu<sub>2</sub>O–Pt/SiC/IrOx photocatalyst and Fe<sup>2+</sup> for CO<sub>2</sub> reduction, while the second chamber with Pt/WO<sub>3</sub> and Fe<sup>3+</sup> for H<sub>2</sub>O oxidation.





This artificial system exhibited photocatalytic performance for CO<sub>2</sub> reduction to HCOOH with a yield of 896.7  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> for the long-term reaction and simultaneous H<sub>2</sub>O oxidation to O<sub>2</sub> with a stoichiometric ratio. These results can be due to both the direct Z-scheme electronic structure of Cu<sub>2</sub>O-Pt/SiC/IrOx and the indirect Z-scheme spatially separated reduction and oxidation units, which greatly prolong lifetime of photogenerated electrons and holes and prevents the backward reaction of products.

#### 4.2.2. Conversion of Acetophenone to Phenylethanol in PMRs

Only few works have appeared till now on the use of a PMR in reduction reactions such as photocatalytic transfer hydrogenation of ketones [57,59]. The reduction of carbonyl compounds, in the corresponding alcohols, plays an important role in organic synthesis [1–4,57,59]. Molinari et al. [57], to develop a sustainable process, studied the photocatalytic hydrogenation of acetophenone to phenylethanol using commercial TiO<sub>2</sub> and homemade Pd/TiO<sub>2</sub> photocatalysts under UV and visible light, with water and formic acid, in batch and membrane reactor. They tested different methods for the substrate addition in the membrane photoreactor finding the best performance when the acetophenone was used as both solvent and reactant (substrate) with improved performance (productivity 4.44 mg  $g^{-1}$  h<sup>-1</sup> vs. 2.96 mg  $g^{-1}$  h<sup>-1</sup> PMR vs batch reactor). The photocatalytic activity in the PMR under visible light irradiation was improved five times by using Pd/TiO<sub>2</sub> (productivity 22.0 mg g<sup>-1</sup>h<sup>-1</sup>). Recently, Lavorato et al. [59] studied the photocatalytic properties of TiO<sub>2</sub>-loaded faujasite (FAU) zeolite and Pd/TiO<sub>2</sub>/FAU in the heterogeneous transfer hydrogenation of AP under UV and visible light in batch and in a membrane reactor. A highly homogeneous dispersion of TiO<sub>2</sub> catalyst particles on the zeolite surface was obtained in the sample TF10P, prepared by using the lowest amount of TiO<sub>2</sub> precursor and isopropanol as solvent. The results showed that Pd doping of TF10P sample gave the photocatalyst Pd\_TF10P active in the visible light. The productivity obtained in the PMR was higher by using Pd\_TF10P [59] (productivity 99.6 mg g<sub>TiO2</sub> <sup>-1</sup> h<sup>-1</sup> vs. 22 mg g<sub>TiO2</sub> <sup>-1</sup> h<sup>-1</sup>) with an extraction percentage of phenylethanol of ca. 25%.

#### 4.3. Partial and Total Oxydations in PMRs

Membrane separation has been studied in partial (e.g., benzene to phenol) or total oxidation (e.g., water treatment) due to its excellent performance, relatively low energetic cost, and nontoxicity [1–4,180–182].

#### 4.3.1. Partial Oxidation of Benzene to Phenol in PMRs

Phenol production is mainly obtained by the three-step cumene process. An interesting alternative is direct benzene oxidation. Many studies have been achieved on this topic, also in membrane reactor, but in general under UV light irradiation [2,37,181]. The photocatalytic approach consists of the unselective oxidation by generation of OH• radicals with formation of by-products because phenol is more reactive than benzene [37,150]. To improve the selectivity for phenol production, some authors reported photocatalytic oxidations combined with a membrane to achieve phenol separation during the photocatalytic reaction thus avoiding further oxidation [37]. These studies use UV light, instead of a greener approach that can be achieved by irradiating the photocatalyst with visible or solar light. For this reason, some authors studied various modification of the photocatalyst to improve its activity under visible light but, until now, only studies in batch reactors (see Section 3.3.4) are reported. In the near future, studies on PMRs using visible light are expected.

#### 4.3.2. Chemical Conversions for Water Treatment in PMRs

Membranes for water purification can offer easily clean water, but some disadvantages are membrane fouling and the necessity of the successive removal, from permeate water, of some contaminants, still contained, with further treatment [183–185]. Various authors proposed the coupling of membrane filtration with photocatalysis to overcome these problems [1,181,185,186].

For example, Ma et al. [185], and Zhang et al. [186], fabricated a membrane via the immobilization of TiO<sub>2</sub> on the surface of a ceramic membrane. This photocatalytic system, with integrated membrane, not only presented improved removal efficiency, but also showed an enhanced fouling resistance during the filtration process, furthermore, the contaminants in water can be degraded by photocatalysis. The majority of reported photocatalytic membranes are applied under UV light irradiation [1–4], but, nowadays, studies on systems operating under solar or visible light are found in literature [180,187,188]. In the following, very recent papers on oxidation reactions and

water treatment in photocatalytic membrane reactors under visible light are reported. Roso et al. [187], investigated the degradation of volatile organic compounds, such as acetaldehyde and methanol, using PVDF electrospun membranes modified with TiO<sub>2</sub>, Ag<sub>2</sub>CO<sub>3</sub> and GO. The results showed a complete degradation of 1600 ppm of acetaldehyde within 15 min and 600 ppm of methanol within 40 min under visible light irradiation employing the PVDF/TiO<sub>2</sub>–Ag<sub>2</sub>CO<sub>3</sub>–GO system. The authors explained the high photoactivity with the presence of the heterojunction formed between Ag<sub>2</sub>CO<sub>3</sub> and TiO<sub>2</sub>, which effectively separated the charge carriers.

Zhang et al. [180], reported the preparation of  $g-C_3N_4$  quantum dots (QDs) assembled into TiO<sub>2</sub> nanotube array (TNA) membranes to obtain a visible-light-driven  $g-C_3N_4$ /TNA membrane. They reported more than 60% of rhodamine B removed from water under visible light irradiation thanks to the synergistic effect of membrane filtration and photocatalysis. Moreover, this type of membrane integrated process showed also an improved anti-fouling ability during filtration of water containing *Escherichia coli*, under visible light irradiation, with a permeate flux 2 times higher than the filtration alone.

The growing increase of the presence of pharmaceutical products and their metabolites as environmental pollutants require advances in wastewater treatment to limit the potential risk they pose to aquatic organisms and human health [153]. Photocatalysis has emerged as a foremost reliable application with high efficiency for degradation of pharmaceuticals due to its ability to destroy organic (mineralize) pollutants, nontoxicity, chemical inertness, and low cost [15,153,170,171,180,188]. Among the various pharmaceuticals, diclofenac (DCF) is a very common synthetic non-steroidal anti-inflammatory drug found in wastewaters. It is an organic pollutant hardly biodegradable, and thus difficult to completely remove by conventional wastewater treatment processes [153]. To enhance DCF removal, very recently, Nguyen et al. [153], studied the performance of visible/N-doped TiO<sub>2</sub> photocatalyst (with and without H<sub>2</sub>O<sub>2</sub> addition to the reaction environment) using a submerged photocatalytic membrane reactor (SMPR) with suspended photocatalyst obtaining best results by adding hydrogen peroxide as oxidant. N-TiO<sub>2</sub> is a promising photocatalyst for wastewater treatment because N is more effective than other dopants (C, S, P) in narrowing the optical bandgap of TiO<sub>2</sub> because of closing energy between N 2p state and O 2p state. The SMPR, Figure 8, was a cylindrical photoreactor (2 L volume) with an immersed tube of a MF ceramic membrane surrounded by five visible lamps of 50 W (420-720 nm). The membrane was connected to a suction pump to collect the treated water and its sampling. The oxygen was continuously fed under the UF membrane.



Figure 8. Submerged photocatalytic membrane reactor (SMPR) set up [153].

The results indicated that by using a higher DCF initial concentration the efficiency of the process decreased, but, by adding H<sub>2</sub>O<sub>2</sub>, the system performance enhanced. The experimental data were found to fit well a pseudo-first-order kinetic model.

Hu et al. [189], designed another PMR system integrated with photocatalyst for wastewater treatment. They used P-doped g-C<sub>3</sub>N<sub>4</sub> (PCN) as photocatalyst, coated on an Al<sub>2</sub>O<sub>3</sub> substrate followed by integration with an inorganic Al<sub>2</sub>O<sub>3</sub> hollow fiber membrane module for use as a PMR. In Figure 9 the PMR configuration is showed: it was built by collecting a Pyrex reactor for batch-type photocatalytic degradation with a 300 W Xe lamp used as the light source to simulate solar irradiation and connecting it to the UF membrane. In this PMR system the photocatalyst, PCN@S is separated from the Al<sub>2</sub>O<sub>3</sub> hollow fiber membrane module. The wastewater (1 L) contained methylene blue (MB), methyl orange (MO) or phenol. The photocatalyst amount of 10 wt% PCN exhibited the highest degradation activity for MB removal under visible irradiation. The PMR exhibited higher efficiency and stability in the removal of MB, MO and phenol. The total organic carbon (TOC) analysis revealed that more than 92% of the phenol was decomposed and mineralized in the PMR, which also had a MB removal efficiency greater than of 90% when repeatedly used for four times.



**Figure 9.** Schematic diagram of the PMR system integrated with inorganic Al<sub>2</sub>O<sub>3</sub> hollow fiber membrane module and PCN@S photocatalyst [189].

Athanasekou et al. [190] studied the efficacy of a hybrid process that included photocatalysis and ultrafiltration to reduce the presence of synthetic dyes in water. They prepared some ceramic UF membranes with deposition of various photocatalysts (TiO<sub>2</sub>, graphene oxide-TiO<sub>2</sub> composites) based nanomaterials on the external and internal (pore) surface of UF mono-channel monoliths. The photocatalytic filtration experiments took place in a patented water purification device in continuous flow conditions, using MB and MO as azo-dye model pollutants, under near-UV/vis and visible light irradiation.

Ashar et al. [191], studied the photocatalytic degradation of RB5 reactive dye under artificial sunlight by using ZnO and Fe<sup>3+</sup>@ZnO nano discs in PMRs. The results showed 88.89% of dye degradation by using ZnO/PMR and 98.34% by using Fe<sup>3+</sup>@ZnO PMR in 180 min. The photocatalytic activity of Fe<sup>3+</sup>@ZnO PMR gradually decreased after the PMR reuse for eight reaction times.

It is known that one of the main problems in membrane purification is the fouling. To this aim, Sun et al. [192], prepared a photocatalytic membrane with good antifouling and self-cleaning ability. They reported the use of an external magnetic field to arrange the magnetic TiO<sub>2</sub>@Ni particles (MNPs) onto the polymeric polyether sulfone (PES) membrane surface that acquired a self-cleaning property under UV light and sunlight radiation. The optimal membrane, after self-cleaning, presented a flux recovery ratio (FRR) of 75.4%, 99.56%, 92.11% and 98.26% for bovine serum albumin (BSA), yeast extract fermentation (YEF), ammonium alginate (SA) and humic acid (HA) solutions, respectively. The group of Lv et al. [193] fabricated a self-cleaning membrane using a mussel-inspired method, that was used with high photocatalytic efficiency in dye degradation under visible light and with hydrogen peroxide. The membrane consisted of a polydopamine (PDA)/polyethyleneimine (PEI) intermediate layer casted on a UF membrane support and a photocatalytic layer made of  $\beta$ -FeOOH nanorods. The wettability enhanced after this treatment (the dynamic water contact angle decreased

from  $60^{\circ}$  to  $20^{\circ}$ ). During the photocatalytic test the authors observed a slight decrease of permeate flux in the initial 2 h, while it recovered to nearly the original value after 6 h of filtration.

Graphene oxide (GO) is a material of particular interest to make membranes for water purification thanks to its hydrophilic surface properties and the special interconnected 2D nanofluidic channels for ion/molecule transport. To improve the photocatalytic response of the photocatalytic membrane, eliminating also the fouling under visible light irradiation, Liu et al. doped the surface of GO and titanate nanotubes (TNTs) with Ag nanoparticles [194]. Ag/GO/TNT membranes exhibited good ability on photocatalytic degradation of MB dye under visible light. They reported that 90% of MB could be degraded after 120 min irradiation. The flux of Ag/GO/TNT membranes, with a ratio of GO and TNT equal to 1:3 and 6% of Ag content, was 34.7 L m<sup>-2</sup> h<sup>-1</sup> which was double compared to some membrane filtration tests without visible light irradiation. Four types of membranes prepared by using a non-toxic solvent and GO nanosheets as a metal-free catalyst, to photoactivate the membrane, were investigated by Alyarnezhad for the degradation of methylene blue (MB<sup>+</sup>) under visible light irradiation (>420 nm) [195]. The incorporation of GO enhanced the mechanical strength of the membranes prepared and their wettability. Moreover, the presence of one hydration layer on the membrane surface limited the fouling decreasing the attachment of pollutants and microorganisms. The results showed a dye removal efficiency of 83.5% under simulated solar light irradiation by using M8 membrane sample, prepared with PVP, PEG and GO (0.125 wt%) in the dope solution, and exposed for 2.5 min to moisture during the VIPS step.

#### 5. Design of Novel PMRs

The use of magnetic materials in the preparation of photocatalyst composites and coating semiconductors on optical fibers can give a significant advancement in potable water treatment. In the last years the development of new materials that incorporate graphene-based semiconductors have been increased for their adsorptive ability towards pharmaceuticals for waste water treatment [196]. Advancements in photocatalytic materials research have allowed the development of various materials, e.g.: adsorbents incorporated in membrane technologies, photocatalysts combined with magnetic material and coated on optical fibers. Magnetic composites can make the removal of the photocatalysts from water easier and more effective reducing the chance that they may accidentally end up in the environment. Moreover, the introduction of magnetic materials in the composite improved their degradative properties [196–199]. Some authors reported the use of magnetic FeNi<sub>3</sub>/SiO<sub>2</sub>/CuS to remove tetracycline [199] while magnetic fluorinated mesoporous graphitic carbon nitride and a magnetic TiO<sub>2</sub>-GO-Fe<sub>3</sub>O<sub>4</sub> [112,197] were used to remove amoxicillin from waste water. Recently, some authors reported various photocatalytic materials loaded on optical fibers [196]. The immobilization of semiconductors on optical fibers is an interesting method for recovering photocatalysts; furthermore, this method allows light to better reach the nanoparticles as less light is absorbed by other particles present in the solution.

A type of composite semiconductor as TiO<sub>2</sub>-rGO coated optical fibers was able to degrade pharmaceutical compounds such as sulfamethoxazole and ibuprofen [200]. Modification of existing potable water treatment plant equipment or processes, including photocatalysts or graphene-based materials in membrane technologies, can significantly enhance the functionality of the membranes, reduce fouling and degrade contaminants. Indeed, the use of TiO<sub>2</sub> alone in polyacrylonitrile membranes was reported to be unsuitable for long-term use [201].

Another type of hollow fiber membrane was studied by Kamaludin et al. [202], for the removal of bisphenol A (BPA) from water under visible light. Today a treatment for the removal of BPA is greatly required because its presence in various water sources has potentially led to numerous adverse effects in humans. The authors reported the preparation of a photocatalytic dual-layer hollow fiber (DLHF) membrane fabricated via co-spinning phase inversion. The resultant N-doped TiO<sub>2</sub> exhibited good optical properties with an obtained band gap of 2.64 eV which presented excellent photocatalytic activity under ultraviolet and visible irradiation. DLHF membranes showed a 90% BPA removal under UV light irradiation while N-doped TiO<sub>2</sub> DLHF removed 81.6% of BPA under visible light irradiation.

An optical-fiber reactor was employed to photocatalytically reduce CO<sub>2</sub> with H<sub>2</sub>O to fuels under UVA artificial light and concentrated natural sunlight [203]. The optical fiber was prepared by coating it with a gel-derived TiO<sub>2</sub>–SiO<sub>2</sub> mixed oxide-based photocatalyst. The insert of Fe atom into the TiO<sub>2</sub>–SiO<sub>2</sub> lattice during the sol–gel process, influenced the visible light absorption and product selectivity. Under UVA, by using Cu–Fe/TiO<sub>2</sub>, the main product was ethylene with the quantum yield of 0.0235%, instead, by using Cu–Fe/TiO<sub>2</sub>–SiO<sub>2</sub> catalyst, methane production was favored with the quantum yield of 0.05%. Under natural sunlight only methane was produced by using both TiO<sub>2</sub>–SiO<sub>2</sub> and Cu–Fe/TiO<sub>2</sub>–SiO<sub>2</sub> catalysts with the production rates of 0.177 and 0.279 mmol  $g_{cat}^{-1}$  h<sup>-1</sup>, respectively.

Some recent systems, reported in the following, despite work under UV light, can help to develop novel PMRs working under visible light. Tugaoen et al. reported the development of a compact reactor, for photocatalytic water treatment, in which TiO<sub>2</sub> was coated on optical fibers by using light-emitting diodes [201]. The TiO<sub>2</sub>/optical fiber flow reactor, schematized in Figure 10, consisted of a Near Clear PVC cylinder with an inner diameter of 1.9 cm and a total length of 18 cm. A peristaltic pump circulated solutions at 5 mL min<sup>-1</sup>, resulting in a 10 min hydraulic retention time within the reactor. This one was connected in series with a 100 mL reservoir in which solutions containing 0.1 mM of pCBA at pH 4.0 were introduced and recirculated through the system. The coated optical fibers LED couple (OF/LED) were inserted into the reactor at the same distance (1 cm). Three configurations OF/LED units connected to a single LED source were examined: (1) an individual fiber, (2) a bundle of three fibers, and (3) a bundle of fifteen fibers. Moreover, the number of OF/LED units inside the reactor was varied from 1 to 5. The use of TiO<sub>2</sub> coated optical fiber bundles reduced the energy requirements to deliver photons and increased available surface area enhancing the oxidative removal performance of the chlorinated pollutant *para*-chlorobenzoic acid (pCBA).



**Figure 10.** (**a**) Scheme of the flow-through coated optical fibers LED (OF/LED) reactor. (**b**) Details of possible configuration and working mechanism of a single fiber [201].

Cheng et al. [204] developed a photocatalytic reactor to improve the performance of the photocatalytic reduction of CO<sub>2</sub>. They used an optofluidic planar microreactor irradiated by a 100 W LED (365 nm) with the light intensity changed by adjusting the distance between the microreactor. The reaction environment was constituted by an aqueous alkaline solution. During tests CO<sub>2</sub> (99.99% purity) was continuously provided to the NaOH solution for 1 h to saturate with CO<sub>2</sub> and to remove dissolved oxygen. Then the CO<sub>2</sub> saturated solution was pumped into the microreactor by a syringe pump. The microreactor was made by a transparent rectangular reaction chamber as the top cover and a porous TiO<sub>2</sub> film coated glass as the bottom substrate. The porous TiO<sub>2</sub> film on the glass slide was formed by the wet spray method. This system presented the following advantages: large surface-area-to-volume ratio, enhanced mass and photon transfer and more uniform light distribution. The performances were evaluated by measuring the concentration of produced methanol to estimate the methanol yield. At high light intensity and NaOH concentration, both the methanol concentration and yield increased. Also, improving the catalyst loading, the performance of the system increased with better results (methanol yield of 454.6 mmol  $g_{cat}^{-1}$  h<sup>-1</sup>) using a liquid flow rate of 50 mL min<sup>-1</sup>, 0.2 M NaOH, and light intensity of 8 mW cm<sup>-2</sup>.

#### 6. Summary and Future Perspective

In the present overview, recent literature on photocatalytic organic synthesis and water treatment under visible light is reported. Previous studies on photocatalytic reduction as well as partial and total oxidation of organics on membrane reactors have shown the great potential of this technology but they ostly involve the use of UV light. In recent years, solar-driven photocatalytic conversion has become very attractive as a means to convert solar energy in a clean and effective way for chemical reactions. For this reason, in this paper we focus on the photocatalytic organic synthesis and water treatment under visible light. To utilize more efficiently the solar energy, several semiconductor materials possessing visible-light- activity have been designed and prepared by many authors. The key point in the design is to expanse the light-harvesting region from UV to visible obtaining photocatalysts active under visible light. The reported recently studies on the innovation and quality enhancement of photocatalytic materials for photocatalytic reactions show the crucial role of the suitable design of the photocatalytic system. In particular: choice of the photocatalyst, photocatalyst design, combination of photocatalysts, doping with noble metals, dye sensitization, etc. to allow to improve the visible light absorption of photocatalyst thus limiting photogenerated chargecarrier problems and increasing yield and selectivity. Photocatalysts based on TiO<sub>2</sub>, CdS, WO<sub>3</sub>, ZnFe<sub>2</sub>O<sub>4</sub>, graphene, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), GQDs and MOFs etc., further modified or doped to improve their visible light absorption seems of particular interest in synthesis and water treatment. Combining photocatalysis with membrane separations, hybrid systems named photocatalytic membrane reactors (PMR) are obtained. Their main advantages are: synergic effect, catalyst reuse, selectivity enhancement, improved anti-fouling ability, lower degradation rate and longer lifetime of polymeric membranes, thanks to the lower energy of visible light. The use of magnetic materials in the preparation of photocatalyst composites, the coating of semiconductors on optical fibers, the use of membrane microreactors, can be promising in synthesis and potable water treatment for the easier removal of the photocatalysts from water with the future perspective to employ visible light. A sustainable process can be obtained by operating PMRs with visible-LED or solar light as clean non-limited energy source and with green photocatalysts. On this aspect, the development of new photocatalysts with high activity under visible light and their application in the various research fields in suitable designed PMRs is an expanding research area.

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# References

- Molinari, R.; Lavorato, C.; Argurio, P.; Szymanski, K.; Darowna, D.; Mozia, S. Overview of Photocatalytic Membrane Reactors in Organic Synthesis, Energy Storage and Environmental Applications. *Catalysts* 2019, 9, 239, doi:10.3390/catal9030239.
- 2. Molinari, R.; Argurio, P.; Lavorato, C. Review on Reduction and Partial Oxidation of Organics in Photocatalytic (Membrane) Reactors. *Curr. Org. Chem.* **2013**, *17*, 2516–2537.
- 3. Molinari, R.; Lavorato, C.; Argurio, P. Recent progress of photocatalytic membrane reactors in water treatment and in synthesis of organic compounds. A review. *Catal. Today* **2017**, *281*, 144–164, doi:10.1016/j.cattod.2016.06.047.
- 4. Lavorato, C.; Argurio, P.; Molinari, R. Hydrogen production and organic synthesis in Photocatalytic Membrane Reactors: A review. *Int. J. Membr. Sci. Technol.* **2020**, *7*, 1–14, doi:10.15379/2410-1869.2020.07.01.01.
- 5. Herrmann, J.M. Heterogeneous photocatalysis: State of the art and present applications. *Top. Catal.* **2005**, 34, 49–65, doi:10.1007/s11244-005-3788-2.
- 6. Xing, X.L.; Tang, S.L.; Hong, H.; Jin, H.G. Concentrated solar photocatalysis for hydrogen generation from water by titania-containing gold nanoparticles. *Int. J. Hydrog. Energy* **2020**, *45*, 9612–9623, doi:10.1016/j.ijhydene.2020.01.197.
- Braslavsky, S.E.; Braun, A.M.; Cassano, A.E.; Emeline, A.V.; Litter, M.I.; Palmisano, L.; Parmon, V.N.; Serpone, N. Glossary of terms used in photocatalysis and radiation catalysis (IUPAC Recommendations 2011) (vol 83, pg 931, 2011). *Pure Appl. Chem.* 2011, *83*, 1215–1215, doi:10.1351/PAC-REC-09-09-36\_errata.
- 8. Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, 238, 37–38.
- 9. Kumar, S.G.; Devi, L.G. Review on Modified TiO2 Photocatalysis under UV/Visible Light: Selected Results and Related Mechanisms on Interfacial Charge Carrier Transfer Dynamics. *J. Phys. Chem. A* 2011, *115*, 13211–13241, doi:10.1021/jp204364a.
- Zhu, L.N.; Meng, L.J.; Shi, J.Q.; Li, J.H.; Zhang, X.S.; Feng, M.B. Metal-organic frameworks/carbon-based materials for environmental remediation: A state-of-the-art mini-review. *J. Environ. Manag.* 2019, 232, 964– 977, doi:10.1016/j.jenvman.2018.12.004.
- Hwangbo, M.; Claycomb, E.C.; Liu, Y.N.; Alivio, T.E.G.; Banerjee, S.; Chu, K.H. Effectiveness of zinc oxideassisted photocatalysis for concerned constituents in reclaimed wastewater: 1,4-Dioxane, trihalomethanes, antibiotics, antibiotic resistant bacteria (ARB), and antibiotic resistance genes (ARGs). *Sci. Total Environ.* 2019, 649, 1189–1197, doi:10.1016/j.scitotenv.2018.08.360.
- 12. Ayodhya, D.; Veerabhadram, G. A review on recent advances in photodegradation of dyes using doped and heterojunction based semiconductor metal sulfide nanostructures for environmental protection. *Mater. Today Energy* **2018**, *9*, 83–113, doi:10.1016/j.mtener.2018.05.007.
- Janssens, R.; Mandal, M.K.; Dubey, K.K.; Luis, P. Slurry photocatalytic membrane reactor technology for removal of pharmaceutical compounds from wastewater: Towards cytostatic drug elimination. *Sci. Total Environ.* 2017, 599, 612–626, doi:10.1016/j.scitotenv.2017.03.253.
- 14. Meng, X.C.; Li, Z.Z.; Zhang, Z.S. Pd-nanoparticle-decorated peanut-shaped BiVO4 with improved visible light-driven photocatalytic activity comparable to that of TiO2 under UV light. *J. Catal.* **2017**, *356*, 53–64, doi:10.1016/j.jcat.2017.09.005.
- 15. Zhi, Y.F.; Ma, S.; Xia, H.; Zhang, Y.M.; Shi, Z.; Mu, Y.; Liu, X.M. Construction of donor-acceptor type conjugated microporous polymers: A fascinating strategy for the development of efficient heterogeneous photocatalysts in organic synthesis. *Appl. Catal. B Environ.* **2019**, *244*, 36–44, doi:10.1016/j.apcatb.2018.11.032.
- Parrino, F.; Bellardita, M.; Garcia-Lopez, E.I.; Marci, G.; Loddo, V.; Palmisano, L. Heterogeneous Photocatalysis for Selective Formation of High-Value-Added Molecules: Some Chemical and Engineering Aspects. ACS Catal. 2018, 8, 11191–11225, doi:10.1021/acscatal.8b03093.
- 17. Di Paola, A.; Bellardita, M.; Megna, B.; Parrino, F.; Palmisano, L. Photocatalytic oxidation of trans-ferulic acid to vanillin on TiO2 and WO3-loaded TiO2 catalysts. *Catal. Today* **2015**, *252*, 195–200, doi:10.1016/j.cattod.2014.09.012.
- Ibhadon, A.O.; Fitzpatrick, P. Heterogeneous Photocatalysis: Recent Advances and Applications. *Catalysts* 2013, 3, 189–218, doi:10.3390/catal3010189.
- 19. Sang, Y.H.; Liu, H.; Umar, A. Photocatalysis from UV/Vis to Near-Infrared Light: Towards Full Solar-Light Spectrum Activity. *Chemcatchem* **2015**, *7*, 559–573, doi:10.1002/cctc.201402812.

- 20. Lavorato, C.; Primo, A.; Molinari, R.; Garcia, H. N-Doped Graphene Derived from Biomass as a Visible-Light Photocatalyst for Hydrogen Generation from Water/Methanol Mixtures. *Chem. A Eur. J.* **2014**, *20*, 187– 194, doi:10.1002/chem.201303689.
- 21. Lavorato, C.; Primo, A.; Molinari, R.; Garcia, H. Natural Alginate as a Graphene Precursor and Template in the Synthesis of Nanoparticulate Ceria/Graphene Water Oxidation Photocatalysts. *Acs Catal.* **2014**, *4*, 497–504, doi:10.1021/cs401068m.
- 22. Gan, R.Z.; Ma, X.H.; Wang, G.R.; Jin, Z.L. CoSe2 Clusters as Efficient Co-Catalyst Modified CdS Nanorod for Enhance Visible Light Photocatalytic H-2 Evolution. *Catalysts* **2019**, *9*, 616, doi:10.3390/catal9070616.
- Serra, A.; Gomez, E.; Philippe, L. Bioinspired ZnO-Based Solar Photocatalysts for the Efficient Decontamination of Persistent Organic Pollutants and Hexavalent Chromium in Wastewater. *Catalysts* 2019, 9, 974, doi:10.3390/catal9120974.
- 24. Wang, Y.; Liu, X.; Han, X.Y.; Godin, R.; Chen, J.L.; Zhou, W.Z.; Jiang, C.R.; Thompson, J.F.; Mustafa, K.B.; Shevlin, S.A.; et al. Unique hole-accepting carbon-dots promoting selective carbon dioxide reduction nearly 100% to methanol by pure water. *Nat. Commun.* **2020**, *11*, 9, doi:10.1038/s41467-020-16227-3.
- 25. Chen, L.N.; Wang, X.W.; Chen, Y.W.; Zhuang, Z.Y.; Chen, F.F.; Zhu, Y.J.; Yu, Y. Recycling heavy metals from wastewater for photocatalytic CO2 reduction. *Chem. Eng. J.* **2020**, *402*, *9*, doi:10.1016/j.cej.2020.125922.
- 26. Lin, W.Y.; Han, H.X.; Frei, H. CO2 splitting by H2O to CO and O-2 under UV light in TiMCM-41 silicate sieve. *J. Phys. Chem. B* 2004, *108*, 18269–18273, doi:10.1021/jp040345u.
- Qin, G.H.; Zhang, Y.; Ke, X.B.; Tong, X.L.; Sun, Z.; Liang, M.; Xue, S. Photocatalytic reduction of carbon dioxide to formic acid, formaldehyde, and methanol using dye-sensitized TiO2 film. *Appl. Catal. B Environ.* 2013, *129*, 599–605, doi:10.1016/j.apcatb.2012.10.012.
- Slamet; Nasution, H.W.; Purnama, E.; Kosela, S.; Gunlazuardi, J. Photocatalytic reduction of CO2 on copper-doped Titania catalysts prepared by improved-impregnation method. *Catal. Commun.* 2005, *6*, 313– 319, doi:10.1016/j.catcom.2005.01.011.
- 29. Mele, G.; Annese, C.; De Riccardis, A.; Fusco, C.; Palmisano, L.; Vasapollo, G.; D'Accolti, L. Turning lipophilic phthalocyanines/TiO2 composites into efficient photocatalysts for the conversion of CO2 into formic acid under UV-vis light irradiation. *Appl. Catal. A Gen.* **2014**, *481*, 169–172, doi:10.1016/j.apcata.2014.05.008.
- 30. Ichikawa, S.; Doi, R. Hydrogen production from water and conversion of carbon dioxide to useful chemicals by room temperature photoelectrocatalysis. *Catal. Today* **1996**, *27*, 271–277, doi:10.1016/0920-5861(95)00198-0.
- 31. Ola, O.; Maroto-Valer, M.M. Review of material design and reactor engineering on TiO2 photocatalysis for CO2 reduction. *J. Photochem. Photobiol. C Photochem. Rev.* **2015**, 24, 16–42, doi:10.1016/j.jphotochemrev.2015.06.001.
- 32. Barba-Nieto, I.; Caudillo-Flores, U.; Fernandez-Garcia, M.; Kubacka, A. Sunlight-Operated TiO2-Based Photocatalysts. *Molecules* **2020**, *25*, 4008 doi:10.3390/molecules25174008.
- 33. Palmisano, G.; Augugliaro, V.; Pagliaro, M.; Palmisano, L. Photocatalysis: A promising route for 21st century organic chemistry. *Chem. Commun.* **2007**, 3425–3437, doi:10.1039/b700395c.
- Molinari, R.; Argurio, P.; Bellardita, M.; Palmisano, L. Photocatalytic Processes in Membrane Reactors. In Membrane Science and Engineering; Drioli, E., Giorno, L., Fontananova, E., Eds.; Elsevier: Oxford, UK, 2017; Volume 3, pp. 101–138.
- 35. Konig, B. Photocatalysis in Organic Synthesis—Past, Present, and Future. *Eur. J. Org. Chem.* 2017, 2017, 1979–1981, doi:10.1002/ejoc.201700420.
- 36. Molinari, R.; Caruso, A.; Argurio, P.; Poerio, T. Degradation of the drugs Gemfibrozil and Tamoxifen in pressurized and de-pressurized membrane photoreactors using suspended polycrystalline TiO2 as catalyst. *J. Membr. Sci.* **2008**, *319*, 54–63, doi:10.1016/j.memsci.2008.03.033.
- 37. Molinari, R.; Caruso, A.; Poerio, T. Direct benzene conversion to phenol in a hybrid photocatalytic membrane reactor. *Catal. Today* **2009**, *144*, 81–86, doi:10.1016/j.cattod.2009.02.034.
- 38. Lewis, N.S. Research opportunities to advance solar energy utilization. *Science* **2016**, *351*, *6*, doi:10.1126/science.aad1920.
- 39. Yoon, T.P.; Ischay, M.A.; Du, J.N. Visible light photocatalysis as a greener approach to photochemical synthesis. *Nat. Chem.* **2010**, *2*, 527–532, doi:10.1038/nchem.687.
- 40. Zeitler, K. Photoredox Catalysis with Visible Light. *Angew. Chem. Int. Ed.* **2009**, *48*, 9785–9789, doi:10.1002/anie.200904056.

- 41. Bian, Z.F.; Tachikawa, T.; Majima, T. Superstructure of TiO2 Crystalline Nanoparticles Yields Effective Conduction Pathways for Photogenerated Charges. *J. Phys. Chem. Lett.* **2012**, *3*, 1422–1427, doi:10.1021/jz3005128.
- 42. Li, J.; Yang, J.H.; Wen, F.Y.; Li, C. A visible-light-driven transfer hydrogenation on CdS nanoparticles combined with iridium complexes. *Chem. Commun.* **2011**, *47*, 7080–7082, doi:10.1039/c1cc11800e.
- 43. Khakpash, N.; Simchi, A.; Jafari, T. Adsorption and solar light activity of transition-metal doped TiO2 nanoparticles as semiconductor photocatalyst. *J. Mater. Sci. Mater. Electron.* **2012**, *23*, 659–667, doi:10.1007/s10854-011-0466-y.
- 44. Li, C.J.; Xu, G.R.; Zhang, B.H.; Gong, J.R. High selectivity in visible-light-driven partial photocatalytic oxidation of benzyl alcohol into benzaldehyde over single-crystalline rutile TiO2 nanorods. *Appl. Catal. B Environ.* **2012**, *115*, 201–208, doi:10.1016/j.apcatb.2011.12.003.
- 45. Palmisano, G.; Addamo, M.; Augugliaro, V.; Caronna, T.; Garcia-Lopez, E.; Loddo, V.; Palmisano, L. Influence of the substituent on selective photocatalytic oxidation of aromatic compounds in aqueous TiO2 suspensions. *Chem. Commun.* **2006**, 1012–1014, doi:10.1039/b515853b.
- 46. Yurdakal, S.; Palmisano, G.; Loddo, V.; Augugliaro, V.; Palmisano, L. Nanostructured rutile TiO2 for selective photocatalytic oxidation of aromatic alcohols to aldehydes in water. *J. Am. Chem. Soc.* **2008**, *130*, 1568–1569, doi:10.1021/ja709989e.
- 47. Palmisano, G.; Garcia-Lopez, E.; Marci, G.; Loddo, V.; Yurdakal, S.; Augugliaro, V.; Palmisano, L. Advances in selective conversions by heterogeneous photocatalysis. *Chem. Commun.* **2010**, *46*, 7074–7089, doi:10.1039/c0cc02087g.
- 48. Yurdakal, S.; Palmisano, G.; Loddo, V.; Alagoz, O.; Augugliaro, V.; Palmisano, L. Selective photocatalytic oxidation of 4-substituted aromatic alcohols in water with rutile TiO2 prepared at room temperature. *Green Chem.* **2009**, *11*, 510–516, doi:10.1039/b819862d.
- 49. Augugliaro, V.; Loddo, V.; Lopez-Munoz, M.J.; Marquez-Alvarez, C.; Palmisano, G.; Palmisano, L.; Yurdakal, S. Home-prepared anatase, rutile, and brookite TiO2 for selective photocatalytic oxidation of 4-methoxybenzyl alcohol in water: Reactivity and ATR-FTIR study. *Photochem. Photobiol. Sci.* **2009**, *8*, 663–669, doi:10.1039/b818353h.
- 50. Augugliaro, V.; Caronna, T.; Loddo, V.; Marci, G.; Palmisano, G.; Palmisano, L.; Yurdakal, S. Oxidation of aromatic alcohols in irradiated aqueous suspensions of commercial and home-prepared ruffle TiO2: A selectivity study. *Chem. A Eur. J.* **2008**, *14*, 4640–4646, doi:10.1002/chem.200702044.
- 51. Augugliaro, V.; Palmisano, L. Green Oxidation of Alcohols to Carbonyl Compounds by Heterogeneous Photocatalysis. *Chemsuschem* **2010**, *3*, 1135–1138, doi:10.1002/cssc.201000156.
- Palmisano, G.; Yurdakal, S.; Augugliaro, V.; Loddo, V.; Palmisano, L. Photocatalytic selective oxidation of 4-methoxybenzyl alcohol to aldehyde in aqueous suspension of home-prepared titanium dioxide catalyst. *Adv. Synth. Catal.* 2007, 349, 964–970, doi:10.1002/adsc.200600435.
- 53. Zhang, M.A.; Chen, C.C.; Ma, W.H.; Zhao, J.C. Visible-Light-Induced Aerobic Oxidation of Alcohols in a Coupled Photocatalytic System of Dye-Sensitized TiO2 and TEMPO. *Angew. Chem. Int. Ed.* **2008**, 47, 9730–9733, doi:10.1002/anie.200803630.
- 54. Higashimoto, S.; Suetsugu, N.; Azuma, M.; Ohue, H.; Sakata, Y. Efficient and selective oxidation of benzylic alcohol by O-2 into corresponding aldehydes on a TiO2 photocatalyst under visible light irradiation: Effect of phenyl-ring substitution on the photocatalytic activity. *J. Catal.* **2010**, *274*, 76–83, doi:10.1016/j.jcat.2010.06.006.
- 55. Chen, Y.J.; Lin, T.S. Enhancement of visible-light photocatalytic efficiency of TiO2 nanopowder by anatase/rutile dual phase formation. *Appl. Sci.* **2020**, *10*, 6353, doi:10.3390/APP10186353.
- 56. Su, R.; Xie, C.; Alhassan, S.I.; Huang, S.; Chen, R.; Xiang, S.; Wang, Z.; Huang, L. Oxygen Reduction Reaction in the Field of Water Environment for Application of Nanomaterials. *Nanomaterials* **2020**, *10*, 1719, doi:10.3390/nano10091719.
- 57. Molinari, R.; Lavorato, C.; Argurio, P. Photocatalytic reduction of acetophenone in membrane reactors under UV and visible light using TiO2 and Pd/TiO2 catalysts. *Chem. Eng. J.* **2015**, 274, 307–316, doi:10.1016/j.cej.2015.03.120.
- 58. Perera, M.; Wijenayaka, L.A.; Siriwardana, K.; Dahanayake, D.; de Silva, K.M.N. Gold nanoparticle decorated titania for sustainable environmental remediation: Green synthesis, enhanced surface adsorption and synergistic photocatalysis. *Rsc Adv.* **2020**, *10*, 29594–29602, doi:10.1039/d0ra05607c.

- Lavorato, C.; Argurio, P.; Mastropietro, T.F.; Pirri, G.; Poerio, T.; Molinari, R. Pd/TiO2 doped faujasite photocatalysts for acetophenone transfer hydrogenation in a photocatalytic membrane reactor. *J. Catal.* 2017, 353, 152–161, doi:10.1016/j.jcat.2017.07.015.
- 60. Mendez, F.J.; Gonzalez-Millan, A.; Garcia-Macedo, J.A. A new insight into Au/TiO2-catalyzed hydrogen production from water-methanol mixture using lamps containing simultaneous ultraviolet and visible radiation. *Int. J. Hydrog. Energy* **2019**, *44*, 14945–14954, doi:10.1016/j.ijhydene.2019.04.131.
- Fang, J.; Cao, S.W.; Wang, Z.; Shahjamali, M.M.; Loo, S.C.J.; Barber, J.; Xue, C. Mesoporous plasmonic Au-TiO2 nanocomposites for efficient visible-light-driven photocatalytic water reduction. *Int. J. Hydrog. Energy* 2012, *37*, 17853–17861, doi:10.1016/j.ijhydene.2012.09.023.
- Hernández, R.; Hernández-Reséndiz, J.R.; Cruz-Ramírez, M.; Velázquez-Castillo, R.; Escobar-Alarcón, L.; Ortiz-Frade, L.; Esquivel, K. Au-tio2 synthesized by a microwave-and sonochemistry-assisted sol-gel method: Characterization and application as photocatalyst. *Catalysts* 2020, 10, 1052, doi:10.3390/catal10091052.
- 63. Shu, Z.; Cai, Y.; Ji, J.; Tang, C.; Yu, S.; Zou, W.; Dong, L. Pt deposites on tio2 for photocatalytic h2 evolution: Pt is not only the cocatalyst, but also the defect repair agent. *Catalysts* **2020**, *10*, 1047, doi:10.3390/catal10091047.
- 64. Reddy, I.N.; Jayashree, N.; Manjunath, V.; Kim, D.; Shim, J. Photoelectrochemical Studies on Metal-Doped Graphitic Carbon Nitride Nanostructures under Visible-Light Illumination. *Catalysts* **2020**, *10*, *983*, doi:10.3390/catal10090983.
- 65. Regulska, E.; Breczko, J.; Basa, A.; Dubis, A.T. Rare-earth metals-doped nickel aluminate spinels for photocatalytic degradation of organic pollutants. *Catalysts* **2020**, *10*, 1003, doi:10.3390/catal10091003.
- 66. Latorre-Sanchez, M.; Lavorato, C.; Puche, M.; Fornes, V.; Molinari, R.; Garcia, H. Visible-Light Photocatalytic Hydrogen Generation by Using Dye-Sensitized Graphene Oxide as a Photocatalyst. *Chem. A Eur. J.* **2012**, *18*, 16774–16783, doi:10.1002/chem.201202372.
- 67. Chiarello, G.L.; Forni, L.; Selli, E. Photocatalytic hydrogen production by liquid- and gas-phase reforming of CH3OH over flame-made TiO2 and Au/TiO2. *Catal. Today* **2009**, *144*, 69–74, doi:10.1016/j.cattod.2009.01.023.
- 68. Hattori, M.; Noda, K. All electrochemical fabrication of a bilayer membrane composed of nanotubular photocatalyst and palladium toward high-purity hydrogen production. *Appl. Surf. Sci.* **2015**, *357*, 214–220, doi:10.1016/j.apsusc.2015.08.236.
- 69. Su, C.Y.; Wang, L.C.; Liu, W.S.; Wang, C.C.; Perng, T.P. Photocatalysis and Hydrogen Evolution of Al- and Zn-Doped TiO2 Nanotubes Fabricated by Atomic Layer Deposition. *Acs Appl. Mater. Interfaces* **2018**, *10*, 33287–33295, doi:10.1021/acsami.8b12299.
- 70. Su, C.Y.; Wang, C.C.; Hsueh, Y.C.; Gurylev, V.; Keic, C.C.; Perng, T.P. Enabling high solubility of ZnO in TiO2 by nanolamination of atomic layer deposition. *Nanoscale* **2015**, *7*, 19222–19230, doi:10.1039/c5nr06264k.
- 71. Su, C.Y.; Wang, C.C.; Hsueh, Y.C.; Gurylev, V.; Kei, C.C.; Perng, T.P. Fabrication of highly homogeneous Al-doped TiO2 nanotubes by nanolamination of atomic layer deposition. *J. Am. Ceram. Soc.* **2017**, *100*, 4988–4993, doi:10.1111/jace.15044.
- 72. Wang, G.; Guo, W.; Xu, D.; Liu, D.; Qin, M. Graphene oxide hybridised TiO<inf>2</inf> for visible light photocatalytic degradation of phenol. *Symmetry* **2020**, *12*, 1420, doi:10.3390/SYM12091420.
- Huang, J.F.; Lei, Y.; Luo, T.; Liu, J.M. Photocatalytic H(2)Production from Water by Metal-free Dyesensitized TiO(2)Semiconductors: The Role and Development Process of Organic Sensitizers. *Chemsuschem* 2020, 34, doi:10.1002/cssc.202001646.
- Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Vonzelewsky, A. Ru(II) polypyridine complexes-photophysics, photochemistry, electrochemistry, and chemi-luminescence. *Coord. Chem. Rev.* 1988, 84, 85–277, doi:10.1016/0010-8545(88)80032-8.
- 75. Li, X.; Shi, J.L.; Hao, H.M.; Lang, X.J. Visible light-induced selective oxidation of alcohols with air by dyesensitized TiO2 photocatalysis. *Appl. Catal. B Environ.* **2018**, *232*, 260–267, doi:10.1016/j.apcatb.2018.03.043.
- 76. He, H.; Chen, A.; Chang, M.; Ma, L.; Li, C. A feasible hydrogen evolution process of water electrolysis assisted by TiO2 nanotube photocatalysis. *J. Ind. Eng. Chem.* **2013**, *19*, 1112–1116, doi:10.1016/j.jiec.2012.12.006.
- 77. Ayati, A.; Ahmadpour, A.; Bamoharram, F.F.; Tanhaei, B.; Manttari, M.; Sillanpaa, M. A review on catalytic applications of Au/TiO2 nanoparticles in the removal of water pollutant. *Chemosphere* **2014**, *107*, 163–174, doi:10.1016/j.chemosphere.2014.01.040.

- Seh, Z.W.; Liu, S.H.; Low, M.; Zhang, S.Y.; Liu, Z.L.; Mlayah, A.; Han, M.Y. Janus Au-TiO2 Photocatalysts with Strong Localization of Plasmonic Near-Fields for Efficient Visible-Light Hydrogen Generation. *Adv. Mater.* 2012, 24, 2310–2314, doi:10.1002/adma.201104241.
- Azami, M.S.; Nawawi, W.I.; Jawad, A.H.; Ishak, M.A.M.; Ismail, K. N-doped TiO2 Synthesised via Microwave Induced Photocatalytic on RR4 Dye Removal under LED Light Irradiation. *Sains Malays.* 2017, 46, 1309–1316, doi:10.17576/jsm-2017-4608-17.
- 80. Ansari, S.A.; Khan, M.M.; Ansari, M.O.; Cho, M.H. Nitrogen-doped titanium dioxide (N-doped TiO2) for visible light photocatalysis. *New J. Chem.* **2016**, *40*, 3000–3009, doi:10.1039/c5nj03478g.
- 81. Zhao, X.; Zhang, Y.; Wen, P.; Xu, G.; Ma, D.; Qiu, P. NH2-MIL-125(Ti)/TiO2 composites as superior visiblelight photocatalysts for selective oxidation of cyclohexane. *Mol. Catal.* **2018**, 452, 175–183, doi:10.1016/j.mcat.2018.04.004.
- Gao, W.; Zhang, W.Y.; Tian, B.; Zhen, W.L.; Wu, Y.Q.; Zhang, X.Q.; Lu, G.X. Visible light driven water splitting over CaTiO3/Pr3+-Y2SiO5/RGO catalyst in reactor equipped artificial gill. *Appl. Catal. B Environ.* 2018, 224, 553–562, doi:10.1016/j.apcatb.2017.10.072.
- 83. Gao, Z.Y.; Liu, N.; Wu, D.P.; Tao, W.G.; Xu, F.; Jiang, K. Graphene-CdS composite, synthesis and enhanced photocatalytic activity. *Appl. Surf. Sci.* 2012, *258*, 2473–2478, doi:10.1016/j.apsusc.2011.10.075.
- 84. Oh, W.C.; Chen, M.; Cho, K.; Kim, C.; Meng, Z.; Zhu, L. Synthesis of Graphene-CdSe Composite by a Simple Hydrothermal Method and Its Photocatalytic Degradation of Organic Dyes. *Chin. J. Catal.* **2011**, *32*, 1577–1583, doi:10.1016/s1872-2067(10)60264-1.
- 85. Zhang, X.F.; Quan, X.; Chen, S.; Yu, H.T. Constructing graphene/InNbO4 composite with excellent adsorptivity and charge separation performance for enhanced visible-light-driven photocatalytic ability. *Appl. Catal. B Environ.* **2011**, *105*, 237–242, doi:10.1016/j.apcatb.2011.04.024.
- Fu, Y.S.; Sun, X.Q.; Wang, X. BiVO4-graphene catalyst and its high photocatalytic performance under visible light irradiation. *Mater. Chem. Phys.* 2011, *131*, 325–330, doi:10.1016/j.matchemphys.2011.09.049.
- 87. Zhou, F.; Shi, R.; Zhu, Y.F. Significant enhancement of the visible photocatalytic degradation performances of gamma-Bi2MoO6 nanoplate by graphene hybridization. *J. Mol. Catal. A Chem.* **2011**, *340*, 77–82, doi:10.1016/j.molcata.2011.03.012.
- 88. Gao, E.; Wang, W.; Shang, M.; Xu, J. Synthesis and enhanced photocatalytic performance of graphene-Bi2WO6 composite. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2887–2893, doi:10.1039/c0cp01749c.
- 89. Abe, R.; Higashi, M.; Domen, K. Facile Fabrication of an Efficient Oxynitride TaON Photoanode for Overall Water Splitting into H-2 and O-2 under Visible Light Irradiation. *J. Am. Chem. Soc.* **2010**, *132*, 11828–11829, doi:10.1021/ja1016552.
- 90. Zhang, G.G.; Lan, Z.A.; Lin, L.H.; Lin, S.; Wang, X.C. Overall water splitting by Pt/g-C3N4 photocatalysts without using sacrificial agents. *Chem. Sci.* **2016**, *7*, 3062–3066, doi:10.1039/c5sc04572j.
- 91. Zhao, H.; Jiang, Z.F.; Xiao, K.M.; Sun, H.L.; Chan, H.S.; Tsang, T.H.; Yang, S.J.; Wong, P.K. Photo-assisted separation of noble-metal-free oxidation and reduction cocatalysts for graphitic carbon nitride nanosheets with efficient photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* **2021**, *280*, 12, doi:10.1016/j.apcatb.2020.119456.
- Mahvelati-Shamsabadi, T.; Goharshadi, E.K. Photostability and visible-light-driven photoactivity enhancement of hierarchical ZnS nanoparticles: The role of embedment of stable defect sites on the catalyst surface with the assistant of ultrasonic waves. *Ultrason. Sonochem.* 2017, 34, 78–89, doi:10.1016/j.ultsonch.2016.05.021.
- 93. Maeda, K.; Teramura, K.; Takata, T.; Hara, M.; Saito, N.; Toda, K.; Inoue, Y.; Kobayashi, H.; Domen, K. Overall water splitting on (Ga1-xZnx)(N1-xOx) solid solution photocatalyst: Relationship between physical properties and photocatalytic activity. *J. Phys. Chem. B* **2005**, *109*, 20504–20510, doi:10.1021/jp053499y.
- 94. Kong, C.; Min, S.X.; Lu, G.X. Dye-Sensitized NiSx Catalyst Decorated on Graphene for Highly Efficient Reduction of Water to Hydrogen under Visible Light Irradiation. *Acs Catal.* **2014**, *4*, 2763–2769, doi:10.1021/cs5006844.
- 95. Weng, B.; Qi, M.Y.; Han, C.; Tang, Z.R.; Xu, Y.J. Photocorrosion Inhibition of Semiconductor-Based Photocatalysts: Basic Principle, Current Development, and Future Perspective. *ACS Catal.* **2019**, *9*, 4642–4687, doi:10.1021/acscatal.9b00313.
- 96. Ning, X.F.; Lu, G.X. Photocorrosion inhibition of CdS-based catalysts for photocatalytic overall water splitting. *Nanoscale* **2020**, *12*, 1213–1223, doi:10.1039/c9nr09183a.

- 97. Chen, W.; Liu, H.; Li, X.Y.; Liu, S.; Gao, L.; Mao, L.Q.; Fan, Z.Y.; Shangguan, W.F.; Fang, W.J.; Liu, Y.S. Polymerizable complex synthesis of SrTiO3:(Cr/Ta) photocatalysts to improve photocatalytic water splitting activity under visible light. *Appl. Catal. B Environ.* **2016**, *192*, 145–151, doi:10.1016/j.apcatb.2016.03.057.
- Latorre-Sanchez, M.; Primo, A.; Garcia, H. P-Doped Graphene Obtained by Pyrolysis of Modified Alginate as a Photocatalyst for Hydrogen Generation from Water-Methanol Mixtures. *Angew. Chem. Int. Ed.* 2013, 52, 11813–11816, doi:10.1002/anie.201304505.
- 99. Patial, S.; Hasija, V.; Raizada, P.; Singh, P.; Singh, A.; Asiri, A.M. Tunable photocatalytic activity of SrTiO3 for water splitting: Strategies and future scenario. *J. Environ. Chem. Eng.* **2020**, *8*, 21, doi:10.1016/j.jece.2020.103791.
- Luo, X.L.; He, G.L.; Fang, Y.P.; Xu, Y.H. Nickel sulfide/graphitic carbon nitride/strontium titanate (NiSig-C3N4/SrTiO3) composites with significantly enhanced photocatalytic hydrogen production activity. *J. Colloid Interface Sci.* 2018, 518, 184–191, doi:10.1016/j.jcis.2018.02.038.
- Stroyuk, O.L.; Kuchmy, S.Y. Heterogeneous Photocatalytic Selective Reductive Transformations of Organic Compounds: A Review. *Theor. Exp. Chem.* 2020, *56*, 143–173, doi:10.1007/s11237-020-09648-0.
- 102. Thang Phan, N.; Dang Le Tri, N.; Van-Huy, N.; Thu-Ha, L.; Vo, D.-V.N.; Quang Thang, T.; Bae, S.-R.; Chae, S.Y.; Kim, S.Y.; Quyet Van, L. Recent Advances in TiO2-Based Photocatalysts for Reduction of CO2 to Fuels. *Nanomaterials* **2020**, *10*, 337, doi:10.3390/nano10020337.
- 103. Wang, C.; Liu, X.; He, W.; Zhao, Y.; Wei, Y.; Xiong, J.; Liu, J.; Li, J.; Song, W.; Zhang, X.; et al. All-solid-state Z-scheme photocatalysts of g-C3N4/Pt/macroporous-(TiO2@carbon) for selective boosting visible-lightdriven conversion of CO2 to CH4. *J. Catal.* 2020, 389, 440–449, doi:10.1016/j.jcat.2020.06.026.
- 104. Luevano-Hipolito, E.; Torres-Martinez, L.M. Dolomite-supported Cu2O as heterogeneous photocatalysts for solar fuels production. *Mater. Sci. Semicond. Process.* **2020**, *116*, 8, doi:10.1016/j.mssp.2020.105119.
- 105. Adekoya, D.O.; Tahir, M.; Amin, N.A.S. g-C3N4/(Cu/TiO2) nanocomposite for enhanced photoreduction of CO2 to CH3OH and HCOOH under UV/visible light. *J. Co2 Util.* **2017**, *18*, 261–274, doi:10.1016/j.jcou.2017.02.004.
- 106. Acharya, R.; Parida, K. A review on TiO2/g-C3N4 visible-light- responsive photocatalysts for sustainable energy generation and environmental remediation. *J. Environ. Chem. Eng.* **2020**, *8*, 21, doi:10.1016/j.jece.2020.103896.
- 107. Wang, C.J.; Zhao, Y.L.; Xu, H.; Li, Y.F.; Wei, Y.C.; Liu, J.; Zhao, Z. Efficient Z-scheme photocatalysts of ultrathin g-C3N4-wrapped Au/TiO2-nanocrystals for enhanced visible-light-driven conversion of CO2 with H2O. *Appl. Catal. B Environ.* 2020, 263, 13, doi:10.1016/j.apcatb.2019.118314.
- 108. Qiu, C.; Bai, S.; Cao, W.; Tan, L.; Liu, J.; Zhao, Y.; Song, Y.F. Tunable Syngas Synthesis from Photocatalytic CO<sub>2</sub> Reduction Under Visible-Light Irradiation by Interfacial Engineering. *Trans. Tianjin Univ.* 2020, 26, 352–361, doi:10.1007/s12209-020-00265-5.
- 109. Lavorato; C.; Argurio, P.; Molinari, R. TiO2and Pd/TiO2as Photocatalysts for Hydrogenation of Ketones and Perspective of Membrane Application. *Int. J. Adv. Res. Chem. Sci.* **2019**, *6*, 33–41, doi:10.20431/2349-0403.0601005.
- 110. Call, A.; Casadevall, C.; Acuna-Pares, F.; Casitas, A.; Lloret-Fillol, J. Dual cobalt-copper light-driven catalytic reduction of aldehydes and aromatic ketones in aqueous media. *Chem. Sci.* **2017**, *8*, 4739–4749, doi:10.1039/c7sc01276d.
- 111. Kohtani, S.; Nishioka, S.; Yoshioka, E.; Miyabe, H. Dye-sensitized photo-hydrogenation of aromatic ketones on titanium dioxide under visible light irradiation. *Catal. Commun.* **2014**, *43*, 61–65, doi:10.1016/j.catcom.2013.09.006.
- 112. Kumar, A.S.K.; You, J.G.; Tseng, W.B.; Dwivedi, G.D.; Rajesh, N.; Jiang, S.J.; Tseng, W.L. Magnetically Separable Nanospherical g-C3N4@Fe3O4 as a Recyclable Material for Chromium Adsorption and Visible-Light-Driven Catalytic Reduction of Aromatic Nitro Compounds. ACS Sustain. Chem. Eng. 2019, 7, 6662– 6671, doi:10.1021/acssuschemeng.8b05727.
- 113. Fueldner, S.; Mild, R.; Siegmund, H.I.; Schroeder, J.A.; Gruber, M.; Koenig, B. Green-light photocatalytic reduction using dye-sensitized TiO2 and transition metal nanoparticles. *Green Chem.* **2010**, *12*, 400–406, doi:10.1039/b918140g.
- 114. Gazi, S.; Ananthakrishnan, R. Metal-free-photocatalytic reduction of 4-nitrophenol by resin-supported dye under the visible irradiation. *Appl. Catal. B Environ.* **2011**, *105*, 317–325, doi:10.1016/j.apcatb.2011.04.025.

- 116. Gogoi, N.; Borah, G.; Gogoi, P.K.; Chetia, T.R. TiO2 supported gold nanoparticles: An efficient photocatalyst for oxidation of alcohol to aldehyde and ketone in presence of visible light irradiation. *Chem. Phys. Lett.* **2018**, *692*, 224–231, doi:10.1016/j.cplett.2017.12.015.
- 117. Lv, Y.; Xu, Z.; Kobayashi, H.; Nakane, K. Novel Pd-loaded urchin-like (NH4)(x)WO3/WO3 as an efficient visible-light-driven photocatalyst for partial conversion of benzyl alcohol. *J. Alloy. Compd.* **2020**, *845*, doi:10.1016/j.jallcom.2020.156225.
- 118. Jiang, C.L.; Wang, H.; Wang, Y.Q.; Ji, H.B. All solid-state Z-scheme CeO2/ZnIn2S4 hybrid for the photocatalytic selective oxidation of aromatic alcohols coupled with hydrogen evolution. *Appl. Catal. B Environ.* **2020**, *277*, 9, doi:10.1016/j.apcatb.2020.119235.
- 119. Guo, W.L.; Zhang, Z.H.; Lin, H.; Cai, L. Z-scheme BiFeO3-CNTs-PPy as a highly effective and stable photocatalyst for selective oxidation of benzyl alcohol under visible-light irradiation. *Mol. Catal.* **2020**, *492*, 12, doi:10.1016/j.mcat.2020.111011.
- 120. Verma, P.; Mori, K.; Kuwahara, Y.; Cho, S.J.; Yamashita, H. Synthesis of plasmonic gold nanoparticles supported on morphology-controlled TiO2 for aerobic alcohol oxidation. *Catal. Today* **2020**, *352*, 255–261, doi:10.1016/j.cattod.2019.10.014.
- Mohammadi, M.; Hadadzadeh, H.; Kaikhosravi, M.; Farrokhpour, H.; Shakeri, J. Selective Photocatalytic Oxidation of Benzyl Alcohol at Ambient Conditions using Spray-Dried g-C3N4/TiO2 Granules. *Mol. Catal.* 2020, 490, doi:10.1016/j.mcat.2020.110927.
- 122. Zhang, F.; Li, J.M.; Wang, H.F.; Li, Y.P.; Liu, Y.; Qian, Q.Z.; Jin, X.; Wang, X.Q.; Zhang, J.H.; Zhang, G.Q. Realizing synergistic effect of electronic modulation and nanostructure engineering over graphitic carbon nitride for highly efficient visible-light H-2 production coupled with benzyl alcohol oxidation. *Appl. Catal. B Environ.* 2020, *269*, 10, doi:10.1016/j.apcatb.2020.118772.
- 123. Contreras, D.; Melin, V.; Marquez, K.; Perez-Gonzalez, G.; Mansilla, H.D.; Pecchi, G.; Henriquez, A. Selective oxidation of cyclohexane to cyclohexanol by BiOI under visible light: Role of the ratio (110)/(001) facet. *Appl. Catal. B Environ.* **2019**, *251*, 17–24, doi:10.1016/j.apcatb.2019.03.058.
- 124. Xiao, Y.; Liu, J.; Wang, H.; Yang, C.; Cheng, H.; Deng, Y.; Cheng, L.; Fang, Y. Photothermal oxidation of cyclohexane by graphene oxide-based composites with high selectivity to KA oil. *Mol. Catal.* **2020**, *493*, doi:10.1016/j.mcat.2020.111103.
- 125. Shiraishi, Y.; Sugano, Y.; Ichikawa, S.; Hirai, T. Visible light-induced partial oxidation of cyclohexane on WO3 loaded with Pt nanoparticles. *Catal. Sci. Technol.* **2012**, *2*, 400–405, doi:10.1039/c1cy00331c.
- 126. Almquist, C.B.; Biswas, P. The photo-oxidation of cyclohexane on titanium dioxide: An investigation of competitive adsorption and its effects on product formation and selectivity. *Appl. Catal. A Gen.* **2001**, *214*, 259–271, doi:10.1016/s0926-860x(01)00495-1.
- Sclafani, A.; Herrmann, J.M. Comparison of the photoelectronic and photocatalytic activities of various anatase and rutile forms of titania in pure liquid organic phases and in aqueous solutions. *J. Phys. Chem.* **1996**, *100*, 13655–13661, doi:10.1021/jp9533584.
- 128. Peng, D.D.; Zhang, Y.; Xu, G.; Tian, Y.; Ma, D.; Qu, P. Synthesis of Multilevel Structured MoS2@Cu/Cu2O@C Visible-Light-Driven Photocatalyst Derived from MOF-Guest Polyhedra for Cyclohexane Oxidation. Acs Sustain. Chem. Eng. 2020, 8, 6622–6633, doi:10.1021/acssuschemeng.9b07212.
- 129. Wang, S.-L.; Wang, L.-L.; Ma, W.-H.; Johnson, D.M.; Fang, Y.-F.; Jia, M.-K.; Huang, Y.-P. Moderate valence band of bismuth oxyhalides (BiOXs, X = Cl, Br, I) for the best photocatalytic degradation efficiency of MC-LR. *Chem. Eng. J.* 2015, 259, 410–416, doi:10.1016/j.cej.2014.07.103.
- 130. Zhao, L.; Liu, Z.; Zhang, X.; Cui, T.; Han, J.; Guo, K.; Wang, B.; Li, Y.; Hong, T.; Liu, J.; et al. Threedimensional flower-like hybrid BiOI-zeolite composites with highly efficient adsorption and visible light photocatalytic activity. *RSC Adv.* **2014**, *4*, 45540–45547, doi:10.1039/c4ra07049f.
- 131. Luo, S.; Tang, C.; Huang, Z.; Liu, C.; Chen, J.; Fang, M. Effect of different Bi/Ti molar ratios on visible-light photocatalytic activity of BiOI/TiO2 heterostructured nanofibers. *Ceram. Int.* **2016**, *42*, 15780–15786, doi:10.1016/j.ceramint.2016.07.043.
- 132. Ciriminna, R.; Fidalgo, A.; Meneguzzo, F.; Parrino, F.; Ilharco, L.M.; Pagliaro, M. Vanillin: The Case for Greener Production Driven by Sustainability Megatrend. *Chemistryopen* **2019**, *8*, 660–667, doi:10.1002/open.201900083.

- 133. Pan, J.; Fu, J.; Lu, X. Microwave-Assisted Oxidative Degradation of Lignin Model Compounds with Metal Salts. *Energy Fuels* **2015**, *29*, 4503–4509, doi:10.1021/acs.energyfuels.5b00735.
- 134. Vedrine, J.C. Heterogeneous Catalysis on Metal Oxides. Catalysts 2017, 7, 341, doi:10.3390/catal7110341.
- 135. Gharehkhani, S.; Zhang, Y.; Fatehi, P. Lignin-derived platform molecules through TEMPO catalytic oxidation strategies. *Prog. Energy Combust. Sci.* 2019, 72, 59–89, doi:10.1016/j.pecs.2019.01.002.
- 136. Camera-Roda, G.; Parrino, F.; Loddo, V.; Palmisano, L. A Dialysis Photocatalytic Reactor for the Green Production of Vanillin. *Catalysts* **2020**, *10*, 326, doi:10.3390/catal10030326.
- 137. Israr, M.; Iqbal, J.; Arshad, A.; Gómez-Romero, P.; Benages, R. Multifunctional MgFe2O4/GNPs nanocomposite: Graphene-promoted visible light driven photocatalytic activity and electrochemical performance of MgFe2O4. *Solid State Sci.* **2020**, doi:10.1016/j.solidstatesciences.2020.106363.
- 138. Parrino, F.; Augugliaro, V.; Camera-Roda, G.; Loddo, V.; Lopez-Munoz, M.J.; Marquez-Alvarez, C.; Palmisano, G.; Palmisano, L.; Puma, M.A. Visible-light-induced oxidation of trans-ferulic acid by TiO2 photocatalysis. J. Catal. 2012, 295, 254–260, doi:10.1016/j.jcat.2012.08.018.
- Al-Hunaiti, A.; Mohaidat, Q.; Bsoul, I.; Mahmood, S.; Taher, D.; Hussein, T. Synthesis and Characterization of Novel Phyto-Mediated Catalyst, and Its Application for a Selective Oxidation of (VAL) into Vanillin under Visible Light. *Catalysts* 2020, *10*, 839, doi:10.3390/catal10080839.
- 140. Fierascu, R.C.; Fierascu, I.; Lungulescu, E.M.; Nicula, N.; Somoghi, R.; Ditu, L.M.; Ungureanu, C.; Sutan, A.N.; Draghiceanu, O.A.; Paunescu, A.; et al. Phytosynthesis and radiation-assisted methods for obtaining metal nanoparticles. J. Mater. Sci. 2020, 55, 1915–1932, doi:10.1007/s10853-019-03713-3.
- Martin-Perales, A.I.; Rodríguez-Padrón, D.; Garcia, A.; Len, C.; de Miguel, G.; Muñoz-Batista, M.J.; Luque, R. Photocatalytic Production of Vanillin over CeOx and ZrO2 Modified Biomass-Templated Titania. *Ind. Eng. Chem. Res.* 2020, *59*, 17085–17093.
- 142. Molinari, R.; Lavorato, C.; Poerio, T. Performance of vanadium based catalyst in a membrane contactor for the benzene hydroxylation to phenol. *Appl. Catal. A Gen.* **2012**, *417*, 87–92, doi:10.1016/j.apcata.2011.12.031.
- 143. Shimizu, K.; Akahane, H.; Kodama, T.; Kitayama, Y. Selective photo-oxidation of benzene over transition metal-exchanged BEA zeolite. *Appl. Catal. A Gen.* **2004**, *269*, 75–80, doi:10.1016/j.apcata.2004.04.001.
- 144. Molinari, R.; Argurio, P.; Poerio, T. Vanadyl acetylacetonate filled PVDF membranes as the core of a liquid phase continuous process for pure phenol production from benzene. *J. Membr. Sci.* **2015**, 476, 490–499, doi:10.1016/j.memsci.2014.12.006.
- 145. Han, J.W.; Jung, J.; Lee, Y.M.; Nam, W.; Fukuzumi, S. Photocatalytic oxidation of benzene to phenol using dioxygen as an oxygen source and water as an electron source in the presence of a cobalt catalyst. *Chem. Sci.* **2017**, *8*, 7119–7125, doi:10.1039/c7sc02495a.
- 146. Xu, B.; Chen, Z.M.; Han, B.; Li, C.C. Glycol assisted synthesis of MIL-100(Fe) nanospheres for photocatalytic oxidation of benzene to phenol. *Catal. Commun.* **2017**, *98*, 112–115, doi:10.1016/j.catcom.2017.04.041.
- 147. Qin, H.; Lin, W.; Zhang, Z.C.; Cheng, J.Y.; Kong, Y. Synthesis of F-TiO2 Nanosheets and its Photocatalytic Oxidation of Benzene to Phenol. *Adv. Eng. Mater. IiiPts* 1–3 **2013**, 750–752, 1160–1163, doi:10.4028/www.scientific.net/AMR.750-752.1160.
- 148. Ye, X.J.; Cui, Y.J.; Qiu, X.Q.; Wang, X.C. Selective oxidation of benzene to phenol by Fe-CN/TS-1 catalysts under visible light irradiation. *Appl. Catal. B Environ.* **2014**, *152*, 383–389, doi:10.1016/j.apcatb.2014.01.050.
- 149. Kurikawa, Y.; Togo, M.; Murata, M.; Matsuda, Y.; Sakata, Y.; Kobayashi, H.; Higashimoto, S. Mechanistic Insights into Visible Light-Induced Direct Hydroxylation of Benzene to Phenol with Air and Water over Pt-Modified WO3 Photocatalyst. *Catalysts* 2020, 10, 557, doi:10.3390/catal10050557.
- 150. Tomita, O.; Ohtani, B.; Abe, R. Highly selective phenol production from benzene on a platinum-loaded tungsten oxide photocatalyst with water and molecular oxygen: Selective oxidation of water by holes for generating hydroxyl radical as the predominant source of the hydroxyl group. *Catal. Sci. Technol.* **2014**, *4*, 3850–3860, doi:10.1039/c4cy00445k.
- 151. Chen, X.F.; Zhang, J.S.; Fu, X.Z.; Antonietti, M.; Wang, X.C. Fe-g-C3N4-Catalyzed Oxidation of Benzene to Phenol Using Hydrogen Peroxide and Visible Light. *J. Am. Chem. Soc.* **2009**, *131*, 11658–11659, doi:10.1021/ja903923s.
- 152. Hosseini, S.M.; Ghiaci, M.; Kulinich, S.A.; Wunderlich, W.; Farrokhpour, H.; Saraji, M.; Shahvar, A. Au-Pd@g-C3N4 as an Efficient Photocatalyst for Visible-Light Oxidation of Benzene to Phenol: Experimental and Mechanistic Study. *J. Phys. Chem. C* **2018**, *122*, 27477–27485, doi:10.1021/acs.jpcc.8b08788.
- 153. Nguyen, T.P.; Tran, Q.B.; Ly, Q.V.; Thanh Hai, L.; Le, D.T.; Tran, M.B.; Ho, T.T.T.; Nguyen, X.C.; Shokouhimehr, M.; Vo, D.V.N.; et al. Enhanced visible photocatalytic degradation of diclofen over N-

doped TiO<sub>2</sub> assisted with H<sub>2</sub>O<sub>2</sub>: A kinetic and pathway study. *Arab. J. Chem.* **2020**, doi:10.1016/j.arabjc.2020.05.023.

- 154. Li, J.Y.; Dong, X.A.; Zhang, G.; Cui, W.; Cen, W.L.; Wu, Z.B.; Lee, S.C.; Dong, F. Probing ring-opening pathways for efficient photocatalytic toluene decomposition. *J. Mater. Chem. A* 2019, *7*, 3366–3374, doi:10.1039/c8ta11627j.
- 155. Li, J.Y.; Cui, W.; Chen, P.; Dong, X.A.; Chu, Y.H.; Sheng, J.P.; Zhang, Y.X.; Wang, Z.M.; Dong, F. Unraveling the mechanism of binary channel reactions in photocatalytic formaldehyde decomposition for promoted mineralization. *Appl. Catal. B Environ.* **2020**, *260*, *7*, doi:10.1016/j.apcatb.2019.118130.
- 156. Buscio, V.; Brosillon, S.; Mendret, J.; Crespi, M.; Gutierrez-Bouzan, C. Photocatalytic Membrane Reactor for the Removal of CI Disperse Red 73. *Materials* **2015**, *8*, 3633–3647, doi:10.3390/ma8063633.
- 157. Khan, S.H.; Pathak, B. Zinc oxide based photocatalytic degradation of persistent pesticides: A comprehensive review. *Environ. Nanotechnol. Monit. Manag.* **2020**, *13*, doi:10.1016/j.enmm.2020.100290.
- 158. Kanan, S.; Moyet, M.A.; Arthur, R.B.; Patterson, H.H. Recent advances on TiO2-based photocatalysts toward the degradation of pesticides and major organic pollutants from water bodies. *Catal. Rev. Sci. Eng.* 2020, 62, 1–65, doi:10.1080/01614940.2019.1613323.
- 159. Khan, S.H.; Pathak, B.; Fulekar, M.H. Synthesis, characterization and photocatalytic degradation of chlorpyrifos by novel Fe: ZnO nanocomposite material. *Nanotechnol. Environ. Eng.* **2018**, *3*, doi:10.1007/s41204-018-0041-3.
- 160. Dehghani, M.H.; Fadaei, A.M. Photocatalytic degradation of organophosphorous pesticide using zinc oxide. *Res. J. Chem. Environ.* 2012, *16*, 104–109.
- Premalatha, N.; Miranda, L.R. Surfactant modified ZnO-Bi2O3 nanocomposite for degradation of lambdacyhalothrin pesticide in visible light: A study of reaction kinetics and intermediates. *J. Environ. Manag.* 2019, 246, 259–266, doi:10.1016/j.jenvman.2019.05.155.
- 162. Nguyen Thi, H.; Nguyen Le Minh, T.; Doan Van, T.; Mai Hung Thanh, T.; Thanh-Dong, P.; Tran Dinh, M.; Hoang Thu, T.; Mai Thien, B.; Minh Viet, N. Monocrotophos pesticide effectively removed by novel visible light driven Cu doped ZnO photocatalyst. *J. Photochem. Photobiol. A Chem.* 2019, 382, doi:10.1016/j.jphotochem.2019.111923.
- 163. Li, W.; Xie, L.; Zhou, L.; Ochoa-Lozano, J.; Li, C.; Chai, X. A systemic study on Gd, Fe and N co-doped TiO2 nanomaterials for enhanced photocatalytic activity under visible light irradiation. *Ceram. Int.* 2020, 46, 24744–24752, doi:10.1016/j.ceramint.2020.06.265.
- 164. Mandal, P.; Nath, K.K.; Saha, M. Efficient Blue Luminescent Graphene Quantum Dots and their Photocatalytic Ability Under Visible Light. *Biointerface Res. Appl. Chem.* 2021, 11, 8171–8178, doi:10.33263/briac111.81718178.
- 165. Liu, X.; Liu, G.; You, S. Effective in-situ reduction of Cr(VI) from leather wastewater by advanced reduction process based on CO2- with visible-light photocatalyst. *Chemosphere* 2020, 263, 127898–127898, doi:10.1016/j.chemosphere.2020.127898.
- 166. Zhang, C.; Liu, G.; Geng, X.; Wu, K.; Debliquy, M. Metal oxide semiconductors with highly concentrated oxygen vacancies for gas sensing materials: A review. *Sens. Actuators A Phys.* 2020, 309, doi:10.1016/j.sna.2020.112026.
- 167. Fang, T.; Yang, X.; Zhang, L.; Gong, J. Ultrasensitive photoelectrochemical determination of chromium(VI) in water samples by ion-imprinted/formate anion-incorporated graphitic carbon nitride nanostructured hybrid. *J. Hazard. Mater.* **2016**, *312*, 106–113, doi:10.1016/j.jhazmat.2016.03.046.
- 168. Cherdchoo, W.; Nithettham, S.; Charoenpanich, J. Removal of Cr(VI) from synthetic wastewater by adsorption onto coffee ground and mixed waste tea. *Chemosphere* **2019**, 221, 758–767, doi:10.1016/j.chemosphere.2019.01.100.
- 169. Wang, W.-Y.; Irawan, A.; Ku, Y. Photocatalytic degradation of Acid Red 4 using a titanium dioxide membrane supported on a porous ceramic tube. *Water Res.* 2008, 42, 4725–4732, doi:10.1016/j.watres.2008.08.021.
- 170. Mozia, S.; Szymanski, K.; Michalkiewicz, B.; Tryba, B.; Toyoda, M.; Morawski, A.W. Effect of process parameters on fouling and stability of MF/UF TiO2 membranes in a photocatalytic membrane reactor. *Sep. Purif. Technol.* **2015**, *142*, 137–148, doi:10.1016/j.seppur.2014.12.047.
- 171. Cao, F.; Liu, H.; Wei, Q.; Zhao, L.; Guo, L. Experimental study of direct solar photocatalytic water splitting for hydrogen production under natural circulation conditions. *Int. J. Hydrog. Energy* **2018**, *43*, 13727–13737, doi:10.1016/j.ijhydene.2017.12.107.

- 172. Lin, Y.-R.; Dizon, G.V.C.; Yamada, K.; Liu, C.-Y.; Venault, A.; Lin, H.-Y.; Yoshida, M.; Hu, C. Sulfur-doped g-C3N4 nanosheets for photocatalysis: Z-scheme water splitting and decreased biofouling. *J. Colloid Interface Sci.* **2020**, *567*, 202–212, doi:10.1016/j.jcis.2020.02.017.
- 173. Nasrollahi, N.; Ghalamchi, L.; Vatanpour, V.; Khataee, A. Photocatalytic-membrane technology: A critical review for membrane fouling mitigation. *J. Ind. Eng. Chem.* **2020**, doi:10.1016/j.jiec.2020.09.031.
- 174. Rodriguez, J.; Puzenat, E.; Thivel, P.X. From solar photocatalysis to fuel-cell: A hydrogen supply chain. *J. Environ. Chem. Eng.* **2016**, *4*, 3001–3005, doi:10.1016/j.jece.2016.06.011.
- 175. Zhao, H.; Yang, X.; Xu, R.; Li, J.; Gao, S.; Cao, R. CdS/NH2-UiO-66 hybrid membrane reactors for the efficient photocatalytic conversion of CO2. *J. Mater. Chem. A* **2018**, *6*, 20152–20160, doi:10.1039/c8ta05970e.
- Pomilla, F.R.; Brunetti, A.; Marci, G.; Garcia-Lopez, E.I.; Fontananova, E.; Palmisano, L.; Barbieri, G. CO2 to Liquid Fuels: Photocatalytic Conversion in a Continuous Membrane Reactor. ACS Sustain. Chem. Eng. 2018, 6, 8743–8753, doi:10.1021/acssuschemeng.8b01073.
- 177. Wang, Y.; Shang, X.; Shen, J.; Zhang, Z.; Wang, D.; Lin, J.; Wu, J.C.S.; Fu, X.; Wang, X.; Li, C. Direct and indirect Z-scheme heterostructure-coupled photosystem enabling cooperation of CO2 reduction and H2O oxidation. *Nat. Commun.* **2020**, *11*, doi:10.1038/s41467-020-16742-3.
- 178. Xu, Y.-F.; Yang, M.-Z.; Chen, B.-X.; Wang, X.-D.; Chen, H.-Y.; Kuang, D.-B.; Su, C.-Y. A CsPbBr3 Perovskite Quantum Dot/Graphene Oxide Composite for Photocatalytic CO2 Reduction. *J. Am. Chem. Soc.* **2017**, *139*, 5660–5663, doi:10.1021/jacs.7b00489.
- 179. Sheng, H.; Oh, M.H.; Osowiecki, W.T.; Kim, W.; Alivisatos, A.P.; Frei, H. Carbon Dioxide Dimer Radical Anion as Surface Intermediate of Photoinduced CO2 Reduction at Aqueous Cu and CdSe Nanoparticle Catalysts by Rapid-Scan FT-IR Spectroscopy. J. Am. Chem. Soc. 2018, 140, 4363–4371, doi:10.1021/jacs.8b00271.
- Zhang, Q.; Quan, X.; Wang, H.; Chen, S.; Su, Y.; Li, Z. Constructing a visible-light-driven photocatalytic membrane by g-C3N4 quantum dots and TiO2 nanotube array for enhanced water treatment. *Sci. Rep.* 2017, 7, doi:10.1038/s41598-017-03347-y.
- 181. Argurio, P.; Fontananova, E.; Molinari, R.; Drioli, E. Photocatalytic membranes in photocatalytic membrane reactors. *Processes* **2018**, *6*, 162, doi:10.3390/pr6090162.
- 182. De Filpo, G.; Pantuso, E.; Armentano, K.; Formoso, P.; Di Profio, G.; Poerio, T.; Fontananova, E.; Meringolo, C.; Mashin, A.I.; Nicoletta, F.P. Chemical Vapor Deposition of Photocatalyst Nanoparticles on PVDF Membranes for Advanced Oxidation Processes. *Membranes* 2018, *8*, 35, doi:10.3390/membranes8030035.
- Mozia, S.; Darowna, D.; Orecki, A.; Wrobel, R.; Wilpiszewska, K.; Morawski, A.W. Microscopic studies on TiO2 fouling of MF/UF polyethersulfone membranes in a photocatalytic membrane reactor. *J. Membr. Sci.* 2014, 470, 356–368, doi:10.1016/j.memsci.2014.07.049.
- 184. Lee, N.H.; Amy, G.; Croue, J.P.; Buisson, H. Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Res.* 2004, 38, 4511–4523, doi:10.1016/j.watres.2004.08.013.
- 185. Ma, N.; Fan, X.; Quan, X.; Zhang, Y. Ag-TiO2/HAP/Al2O3 bioceramic composite membrane: Fabrication, characterization and bactericidal activity. *J. Membr. Sci.* 2009, 336, 109–117, doi:10.1016/j.memsci.2009.03.018.
- 186. Zhang, H.; Quan, X.; Chen, S.; Zhao, H. Fabrication and characterization of silica/titania nanotubes composite membrane with photocatalytic capability. *Environ. Sci. Technol.* **2006**, *40*, 6104–6109, doi:10.1021/es060092d.
- 187. Roso, M.; Boaretti, C.; Bonora, R.; Modesti, M.; Lorenzetti, A. Nanostructured Active Media for Volatile Organic Compounds Abatement: The Synergy of Graphene Oxide and Semiconductor Coupling. *Ind. Eng. Chem. Res.* 2018, 57, 16635–16644, doi:10.1021/acs.iecr.8b04134.
- 188. Horovitz, I.; Avisar, D.; Baker, M.A.; Grilli, R.; Lozzi, L.; Di Camillo, D.; Mamane, H. Carbamazepine degradation using a N-doped TiO2 coated photocatalytic membrane reactor: Influence of physical parameters. J. Hazard. Mater. 2016, 310, 98–107, doi:10.1016/j.jhazmat.2016.02.008.
- 189. Hu, C.; Wang, M.-S.; Chen, C.-H.; Chen, Y.-R.; Huang, P.-H.; Tung, K.-L. Phosphorus-doped g-C3N4 integrated photocatalytic membrane reactor for wastewater treatment. *J. Membr. Sci.* **2019**, *580*, 1–11, doi:10.1016/j.memsci.2019.03.012.
- 190. Athanasekou, C.P.; Moustakas, N.G.; Morales-Torres, S.; Pastrana-Martinez, L.M.; Figueiredob, J.L.; Faria, J.L.; Silva, A.M.T.; Dona-Rodriguez, J.M.; Romanos, G.E.M.; Falaras, P. Ceramic photocatalytic membranes

for water filtration under UV and visible light. *Appl. Catal. B Environ.* **2015**, *178*, 12–19, doi:10.1016/j.apcatb.2014.11.021.

- 191. Ashar, A.; Bhatti, I.A.; Ashraf, M.; Tahir, A.A.; Aziz, H.; Yousuf, M.; Ahmad, M.; Mohsin, M.; Bhutta, Z.A. Fe3+ @ ZnO/polyester based solar photocatalytic membrane reactor for abatement of RB5 dye. *J. Clean. Prod.* 2020, 246, doi:10.1016/j.jclepro.2019.119010.
- 192. Sun, T.; Liu, Y.; Shen, L.; Xu, Y.; Li, R.; Huang, L.; Lin, H. Magnetic field assisted arrangement of photocatalytic TiO2 particles on membrane surface to enhance membrane antifouling performance for water treatment. *J. Colloid Interface Sci.* **2020**, *570*, 273–285, doi:10.1016/j.jcis.2020.03.008.
- 193. Lv, Y.; Zhang, C.; He, A.; Yang, S.-J.; Wu, G.-P.; Darling, S.B.; Xu, Z.-K. Photocatalytic Nanofiltration Membranes with Self-Cleaning Property for Wastewater Treatment. *Adv. Funct. Mater.* **2017**, *27*, doi:10.1002/adfm.201700251.
- 194. Liu, G.; Han, K.; Zhou, Y.; Ye, H.; Zhang, X.; Hu, J.; Li, X. Facile Synthesis of Highly Dispersed Ag Doped Graphene Oxide/Titanate Nanotubes as a Visible Light Photocatalytic Membrane for Water Treatment. *ACS Sustain. Chem. Eng.* **2018**, *6*, 6256–6263, doi:10.1021/acssuschemeng.8b00029.
- 195. Alyarnezhad, S.; Marino, T.; Parsa, J.B.; Galiano, F.; Ursino, C.; Garcia, H.; Puche, M.; Figoli, A. Polyvinylidene Fluoride-Graphene Oxide Membranes for Dye Removal under Visible Light Irradiation. *Polymers* **2020**, *12*, 1509, doi:10.3390/polym12071509.
- 196. Fanourakis, S.K.; Pena-Bahamonde, J.; Bandara, P.C.; Rodrigues, D.F. Nano-based adsorbent and photocatalyst use for pharmaceutical contaminant removal during indirect potable water reuse. *NPJ Clean Water* **2020**, *3*, doi:10.1038/s41545-019-0048-8.
- 197. Li, Q.; Kong, H.; Li, P.; Shao, J.; He, Y. Photo-Fenton degradation of amoxicillin via magnetic TiO2-graphene oxide-Fe3O4 composite with a submerged magnetic separation membrane photocatalytic reactor (SMSMPR). *J. Hazard. Mater.* **2019**, *373*, 437–446, doi:10.1016/j.jhazmat.2019.03.066.
- 198. Sun, Q.; Hong, Y.; Liu, Q.; Dong, L. Synergistic operation of photocatalytic degradation and Fenton process by magnetic Fe3O4 loaded TiO2. *Appl. Surf. Sci.* **2018**, *430*, 399–406, doi:10.1016/j.apsusc.2017.08.085.
- 199. Nasseh, N.; Taghavi, L.; Barikbin, B.; Nasseri, M.A. Synthesis and characterizations of a novel FeNi3/SiO2/CuS magnetic nanocomposite for photocatalytic degradation of tetracycline in simulated wastewater. *J. Clean. Prod.* **2018**, *179*, 42–54, doi:10.1016/j.jclepro.2018.01.052.
- 200. Lin, L.; Wang, H.; Xu, P. Immobilized TiO2-reduced graphene oxide nanocomposites on optical fibers as high performance photocatalysts for degradation of pharmaceuticals. *Chem. Eng. J.* **2017**, *310*, 389–398, doi:10.1016/j.cej.2016.04.024.
- 201. Tugaoen, H.O.N.; Garcia-Segura, S.; Hristovski, K.; Westerhoff, P. Compact light-emitting diode optical fiber immobilized TiO2 reactor for photocatalytic water treatment. *Sci. Total Environ.* **2018**, *613*, 1331–1338, doi:10.1016/j.scitotenv.2017.09.242.
- 202. Kamaludin, R.; Rasdi, Z.; Othman, M.H.D.; Abdul Kadir, S.H.S.; Mohd Nor, N.S.; Khan, J.; Wan Mohamad Zain, W.N.I.Z.; Ismail, A.F.; A Rahman, M.; Jaafar, J. Visible-Light Active Photocatalytic Dual Layer Hollow Fiber (DLHF) Membrane and Its Potential in Mitigating the Detrimental Effects of Bisphenol A in Water. *Membranes* 2020, *10*, 32, doi:10.3390/membranes10020032.
- 203. Nguyen, T.-V.; Wu, J.C.S. Photoreduction of CO2 to fuels under sunlight using optical-fiber reactor. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 864–872, doi:10.1016/j.solmat.2008.02.010.
- 204. Cheng, X.; Chen, R.; Zhu, X.; Liao, Q.; An, L.; Ye, D.; He, X.; Li, S.; Li, L. An optofluidic planar microreactor for photocatalytic reduction of CO2 in alkaline environment. *Energy* **2017**, *120*, 276–282, doi:10.1016/j.energy.2016.11.081.

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